PERCHLORIC ACID AND PERCHLORATES

by

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Dedicated to the memory of

G. FREDERICK SMITH

An inspiring mentor, zealous researcher, delightful raconteur,

and faithful friend.

ABOUT THE AUTHOR

Alfred A. Schilt is Professor of Chemistry at Northern Illinois University where he has taught and conducted research in analytical chemistry since 1962. He completed both his undergraduate studies and a masters degree at the University of Colorado before joining the Eastman Kodak Company as an analytical chemist in 1951. Two years later he resumed graduate studies at the University of Illinois where, under the enthusiastic direction of Professor G. Frederick Smith, he developed strong abiding interests in perchloric acid and perchlorate chemistry, spectrophotometric reagents for trace metal determinations, and applications of coordination chemistry in chemical analysis. After receiving his doctorate in 1956 he taught at the University of Michigan until 1962 when he joined the faculty at Northern Illinois University. In addition to numerous research articles, he is the author of "Analytical Applications of 1,10-Phenanthroline and Related Compounds" published by Pergamon Press in 1969 and co-author of "The Copper Reagents: Cuproine, Neocuproine, Bathocuproine" published by The G. Frederick Smith Chemical Company in 1972.

PREFACE

This monograph is intended to serve as a ready, single source of useful information on the chemistry and applications of perchloric acid and perchlorate compounds. It should also prove helpful to those who would contribute further to the knowledge and utilization of these versatile and intriguing compounds. To this end a thorough search has been made of the literature up to and including publications in 1977. Most, if not all, of the pertinent references are cited. This approach, coupled with a desire for conciseness, has precluded an in-depth treatment of many of the topics. Many papers related to the study of the compounds for use in explosives and propellant mixtures have been omitted. Also omitted for the most part are references to research articles that employed or dealt only marginally with perchloric acid or its salts.

Over the more than 160 years since its inception an aura of fear highlighted by general ignorance or lack of reliable information has surrounded perchloric acid chemistry. Thanks to the pioneering efforts and energies of scientists such as G. Frederick Smith, H. H. Willard, and their many devoted students, perchloric acid and its compounds are now widely and effectively employed. Fear and ignorance have given way to respect and understanding, with due regard for appropriate safety measures. It is sincerely hoped that this monograph will help disseminate the knowledge and safeguards to enable others to put perchloric acid and its derivatives safely and effectively to work in solving their particular problems.

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CONTENTS

CHAPTER I

INTRODUCTION

Historical Highlights

The first preparation of a perchlorate compound was described by Count Friederich von Stadion in a paper entitled "Von den Verbindungen des Chlorine mit dem Sauerstoff", published in 1816.[1] He obtained a new salt, which he called "oxygenated potassium chlorate", as a water-insoluble residue from a mixture of potassium chlorate and concentrated sulfuric acid which had been allowed to stand for 24 hours with frequent agitation. In the same paper he also described obtaining "oxygenated chloric acid" by distilling a mixture of the new salt with its own weight of sulfuric acid (diluted with one-third its weight of water) to 140°, collecting the white vapors that condense in the receiver as a liquid acid. His "liquid acid" was undoubtedly an aqueous solution containing approximately 70% by weight perchloric acid. In a subsequent 1818 paper,[2] Stadion described electrolytic methods for preparation of "oxygenated chloric acid" and "oxygenated potassium chlorate".

Important contributions were made in the early 1830's by G. S. Serullas who prepared ammonium perchlorate, a number of metal perchlorates, and a solid form of perchloric acid (mistaken for the anhydrous acid but later identified as the monohydrate).[3-5] Serullas also introduced the term "perchlorate", using it interchangeably with Stadion's term "oxychlorate".

In the thirty-year period following the work reported by Serullas, a number of significant papers appeared describing new preparations of perchlorates and perchloric acid. These included contributions by Berzelius in 1835,[6] by Penny in 1840,[7] and by Kolbe in 1862.[8] The preparation of ethyl perchlorate, an extremely hazardous explosive, was reported in 1841 by Hare and Boye.[9] Anhydrous perchloric acid, another very explosive substance, was prepared in 1862 by Roscoe,[10] who also correctly identified the solid acid obtained by Serullas as the monohydrate.[11]

1

The explosive nature of certain perchlorates undoubtedly discouraged many from undertaking further studies. Still others were attracted by the possible commercialization of perchlorates for use in pyrotechnics and explosives. For example, Swedish patents were issued to O. F. Carlson in 1892[12] and 1897[13] relating to the manufacture of explosives containing perchlorates. The first commercial perchlorate plant was constructed in 1893 at Mansbo, Sweden. Production problems were numerous and slow to be resolved, but by 1904 the plant was producing ammonium perchlorate on an efficient, regular basis.[14] Not long afterwards manufacture of sodium, potassium, and ammonium perchlorates began in other countries, notably France, Switzerland, Germany and the United States. Production was pushed to maximum levels during World Wars I and II. Instead of falling as it did after World War I, production of ammonium perchlorate continued to grow after 1945, increasing phenomenally in the 1950's because of its usefulness in solid rocket propellants.[14] The remarkable commercial growth for perchlorates from 1910 to the present was accompanied or preceded quite naturally by comparable growth in research. Numerous patents were granted, and countless research publications appeared. Research activity, as evidenced by rate of publication, continues strong to this day.

In reviewing the history of any endeavor the contributions of certain individuals can be seen clearly in retrospect to have influenced significantly further progress and work by others. In addition to recognizing the pioneering efforts of Stadion, Serullas and Roscoe, any historical account of perchloric acid and perchlorates should include at least mention of the persons and contributions cited in the following sentences. Isolation of the anhydride of perchloric acid, Cl_2O_7, was achieved by A. Michael and W. T. Conn in 1900.[15] Extensive measurements of physical properties of perchloric acid-water mixtures were reported in 1902 by H. J. van Wyk leading to the identification of five separate hydrates.[16] In 1912, H. H. Willard of the University of Michigan described a convenient and practical method for the preparation of perchloric acid from ammonium perchlorate.[17] Assisted by various graduate students, Professor Willard made a number of significant contributions to perchlorate chemistry in the course of his long and remarkably productive career.[18] Possibly the most significant influence that Willard exerted on the advancement of perchlorate chemistry was to interest G. Frederick Smith, one of his first graduate students, to undertake his doctoral research on the subject. From his earliest publication with Willard in 1922 to his last professional publications in 1966, and even up to his death in 1976, Smith never lost his curiosity and enthusiasm for perchlorate chemistry research. With over 60 research papers and publications devoted to the subject, he had truly a lifelong love affair with perchlorate chemistry. In addition to advancing the use of perchloric acid and perchlorates in chemical analysis, Professor Smith carried out fundamental studies, devised new preparation procedures, and founded the chemical company that bears his name and has provided perchloric acid and perchlorates to the scientific community since 1928.[19]

In the early 1930's Ernest Kahane of Paris, France published a number of important papers describing the use of perchloric acid for the total destruction of organic and biological matter prior to determination of mineral constituents. Many investigations and applications followed after Kahane's original publication.[20] More recent contributions to perchlorate chemistry include the preparation of perchloryl fluoride by Bode and Klesper[21] and the preparation of chlorine and bromine perchlorates by Schack, Pilpovich, and Wilson.[22] These perchloric acid derivatives have proven useful in organic synthesis.

Question of Natural Occurence

The discovery of small amounts of perchlorates in natural deposits of nitrates in Chile was reported by Beckurts in 1886.[23] This was confirmed a number of years later by various groups of investigators concerned with the possible harmful effects of perchlorate in Chilean nitrate used as plant food.[24-27] In 1896 Sjollema reported finding potassium perchlorate as a contaminate of Chile saltpeter in amounts ranging from 0 to 6.79%, varying even within the same lot.[25] Maschhaupt found a maximum perchlorate content of 1.5% in crude and about 1% in refined saltpeter.[27] Questions as to

how the perchlorate was produced by natural means and why perchlorate has been found naturally only in Chilean saltpeter remain disturbingly unanswered. It is possible that the answers could provide new insights into geological and biological processes and even lead to a new method of preparation of perchlorates.

Discovery of perchlorate in sea water was reported in 1958 by Baas-Becking, Haldane, and Izard,[28] who found levels of 10 to 1000 ppm ClO_4 in samples collected at various localities. Their findings have not been substantiated but instead rather strongly refuted by others. An extensive study by Greenhalgh and Riley[29] indicated no detectable concentration of perchlorate in any of over 30 surface and deep-water samples collected from both northern and southern hemispheres[30] They attributed the earlier findings of Baas-Becking and coworkers to chloride interference. Johannesson[31] found no evidence of naturally occuring perchlorates in samples of fresh-seawater taken 50 miles apart off the coast of Wellington, New Zealand in 1960. At least two other groups have reported the absence of detectable levels of perchlorate in sea water samples, based upon highly sensitive analytical procedures.[32-33] Thus it appears that perchlorate is not an important natural constituent of sea water.

Structure and Properties of Perchlorate Ion

X-ray diffraction measurements on crystalline hydronium perchlorate by Lee and Carpenter[34] indicate that the perchlorate ion has nearly perfect tetrahedral geometry and an average Cl-O bond distance of 1.42 Å. In water its limiting conductance is 67.32 ± 0.06.[35] A difference in molar refractive power between perchlorate ion and chloride ion of 6.66 ± 0.06 has been deducted from refractive index measurements of their aqueous solutions.[36] The standard enthalpy of formation of the perchlorate ion in infinitely dilute aqueous solution at 25° has been determined by two different groups of investigators; their results —30.53 ± 0.20[37] and —30.87 ± 0.07 kcal/mole[38] are in close agreement.

X-ray photoelectron spectra[39] and fluorescence spectra[40] have been investigated to study the bonding and electronic structure of the perchloric anion. The results indicate that the

3d-orbitals of chlorine participate in the $3d_\pi(Cl)-2p_\pi(O)$ and $3d_\sigma(Cl)-2s(O)$ bonds. The relative contributions of the chlorine 3d-orbitals to the 6- and II- bond levels were evaluated by comparing relative intensities in the L-spectrum of chlorine.[40]

The hydration number of the perchlorate ion has an average value of 4, according to Symons' and Waddington[41] who based their determination upon Raman and infrared spectra of aqueous solutions. They found a similar value for the fluoroborate anion. It appears that each oxygen atom, or fluoride atom in the case of fluoroborate, may be hydrogen bonded by a separate water molecule. Hydration of perchlorate ions in nitrobenzene has been studied using cryoscopic measurements to estimate the value of the first hydration constant.[42] Solvation in methanolic solutions has also been studied by low temperature infrared spectroscopy.[43] Raman spectra of various aqueous perchlorate solutions have been interpreted and evaluated as a function of concentration to study the state of perchloric ions and their interactions with metal ions.[44]

The effect of perchlorate ions on the hydrogen bonded structure of water has been examined by infrared spectrometry.[45-46] Strong evidence of the breaking of water structure by perchlorate ions was found with the observation that the optical density of the 2100 cm^{-1} band (combination band of H_2O) decreases with increasing perchlorate ion concentration, while that of the 3590 cm^{-1} band (fundamental band of H_2O) increases. No detectable absorption was observed in the 4000-600 cm^{-1} region indicative of hydrogen bonding between water and perchlorate ion, and the fundamental band due to perchlorate ion was unaltered. This suggests that the interaction which causes the water structure to be altered is purely ionic.[45]

Nuclear magnetic resonance studies of perchlorate solutions have provided some insights concerning the interactions of perchlorate ions with solvent and with metal cations. Berman and Stengle[47] found that free perchlorate ions in solution have a longer relaxation time than in a contact ion-pair with cations, as indicated by NMR line widths for chlorine-35. They report that the tendency for perchlorate ions to form contact ion-pairs is favored by high charge to radius ratio of cation, low dielectric constant of solvent, and

low basic strength of solvent. Craighead and Bryant[48] found evidence of weak complexation between manganous and perchlorate ions. Based upon chlorine-35 NMR relation time measurements they estimated an exchange rate of 3×10^4 to 3.6×10^7 sec^{-1} for the perchlorate-manganous ion exchange process. Quadrapole relaxation studies of perchlorate and other tetrahedral ions in aqueous solution have been reported also by Reimarsson and coworkers.[49] A proton magnetic resonance study of the interaction of perchlorates with anhydrous perchloric acid has provided evidence of hydrogen bonded $H(ClO_4)_2^-$ anion formation.[50]

Although the basicity of the perchlorate ion is exceedingly weak, it is capable of metal ion complexation in the absence of excessive competition by solvent or other ligands. Considerable evidence now supports this once widely doubted fact.[51,52] Further details are provided in Chapter III.

Oxidation-reduction and other chemical properties of the perchlorate ion are described together with those of the acid and other perchlorate compounds in the chapters that follow.

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CHAPTER II

PREPARATION AND PROPERTIES OF PERCHLORIC ACID

AQUEOUS PERCHLORIC ACID

Preparation

Perchloric acid was first synthesized by von Stadion[1,2] in 1816 by vacuum distillation of a mixture of sulfuric acid and potassium chlorate, and by electrolysis of a saturated aqueous solution of chlorine dioxide. Numerous other methods have been devised since, however the most important commercial ones are based upon either the Kreider-Mathers[3] or the Willard[4] method. These and other methods, classified as to type, are described below.

Electrosynthesis. Electrolytic oxidation of hydrochloric acid to perchloric acid, as described by Walker[5] in 1918 and in greater detail by Goodwin and Walker[6] in 1921, proved relatively inefficient for commercial purposes. Production of chlorine rather than perchloric acid is favored at higher concentrations of hydrochloric acid, so it is necessary to employ very dilute (0.1-0.5 N) solutions and thus extensive evaporation to concentrate the product. Some improvements were forthcoming. Rakov and coworkers[7] found that (1) perchloric acid formation begins at 2.4 V and reaches a maximum value at 2.8-2.9 V, (2) lowering the temperature to —20° significantly accelerates the process, and (3) concentration changes of chloride ion from 0.5 to 1.8 N and of perchlorate ion from 3 to 8 N are without effect except for decreased current efficiency at the highest concentration of hydrochloric and perchloric acid. In another study, Rakov et al.[8] found that platinum anodes afford higher yields of perchloric acid than did Pt-Ti or Pt-Ta bianodes. Rakov and Shimonis,[9] in a patent granted in 1976, claim increased current efficiency is attained in the electrosynthesis of perchloric acid from 1 to 4 N hydrochloric acid by using an iridium anode at a potential of 2.9-3.3 V and a temperature at —5 to —30°.

Preparation by anodic oxidation of chlorine has been investigated.[10] At platium electrodes a reaction apparently occurs between adsorbed chlorine and active oxygen which leads to formation of perchloric acid through an adsorbed in-

termediate product.[11] Lead dioxide anodes are especially effective, particularly if sodium flouride is added to the electrolyte.[12]

Electrolytic oxidation of chlorates was investigated by Newman and Mathers.[13] Using a two-diaphragm, three-compartment cell with a platinum anode and iron cathode they were able to obtain an aqueous solution of about 2 N perchloric acid prior to concentrating by evaporation.

Double-decomposition. A solution of perchloric acid can be made by warming an aqueous solution of potassium perchlorate with a small excess of hydrofluosilicic acid, H_2SiF_6, for an hour, and filtering the cooled liquid.[14,15] The slight excess of H_2SiF_6 can be removed by adding a little barium perchlorate or chloride. Another preparation involves decomposition of barium perchlorate with sulfuric acid to yield insoluble barium sulfate and perchloric acid.[16] Kreider[17] prepared an aqueous solution of perchloric acid by treating sodium perchlorate with an excess of concentrated hydrochloric acid, filtering off the sparingly soluble sodium chloride, and heating to 135° to drive off the excess hydrochloric acid. Mathers[18] investigated the Kreider procedure and provided additional procedural details. The Kreider-Mathers method of preparation proved suitable for commercial use and led to the Pernet process,[19] patented in 1946, which provides for continuous operation and nearly automatic control.

A mixture of potassium perchlorate and sulfuric acid when distilled in a current of steam yields an aqueous solution of perchloric acid, contaminated by sulfuric acid, which must be redistilled or treated with barium carbonate to remove sulfate.[20] A much superior method, devised by Willard,[4] involves treatment of ammonium perchlorate with an excess of a mixture of nitric and hydrochloric acid, giving rise to the approximate over-all reaction as follows:

34 NH_4ClO_4 + 36 HNO_3 + 8 HCl → 36 $HClO_4$ + 4 Cl_2 + 35 N_2O + 73 H_2O. Gaseous products and any excess acid reactants are eliminated on heating to concentrate the perchloric acid to its constant boiling composition. Yields in excess of 99%, approaching theoretical, were obtained by Willard.

Chemical Oxidation. Ozone can be used to oxidize hypochlorous[21] and chloric acid[22] to perchloric acid. Patents have been issued for the production of perchlorates and perchloric acid by ozone treatment of chlorates in $HClO_4$[23] and of gaseous mixtures of water and chlorine or hydrogen chloride irradiated with 2537 Å.[24]

Chloric acid undergoes self-oxidation, especially if concentrated, decomposing into perchloric and chlorous acids.[25] Serullas obtained perchloric acid in low yield from thermal decomposition of chloric acid.[26]

Preparation procedures for perchloric acid and perchlorates by oxidation of chloric acid or chlorates on heating with silver oxide[27] or by oxidation with lead dioxide in 55-70% H_2SO_4[28] have been reported but appear to afford little advantage.

Purification

Aqueous solutions of perchloric acid can be concentrated by boiling at atmospheric pressure to 203°, at which point an azeotropic solution is attained containing 72.4% $HClO_4$. For purification by distillation it is necessary to employ reduced pressures (below 200 mm) to avoid partial decomposition to chlorine, chlorine oxides and oxygen. Distillation procedures are described in papers by Mathers,[3] Willard,[4] and others.[29-31]

High-purity perchloric acid (70% by weight), greatly diminished in trace metal content, can be conveniently prepared by a sub-boiling distillation method developed at the National Bureau of Standards.[32] A production rate of about 600 ml of perchloric acid per day was achieved using a pure quartz sub-boiling still. Analysis revealed the presence of 16 ppb total impurity elements as opposed to 3400 ppb for the ACS grade starting acid and 100 ppb for a commercial high-purity acid. Using a similar appartus, but with a constant-level feed-control device, other workers[33] decreased lead impurities in 70% perchloric acid to levels of 0.2-0.4 ppb in a single pass.

An interesting method for removal of impurities from 1 M perchloric acid for use as a supporting electrolyte has been described,[34] based upon adsorptive and electroctive properties of a column of platinum sponge held at a fixed potential.

Physical Properties

Extensive measurements have been made of the physical properties of aqueous solutions of perchloric acid, particu-

larly by H. J. Van Wyk and by L. H. Brickwedde. These are summarized briefly with literature references in the following paragraphs, and many of the results are compiled in Tables 1 through 8.

Densities of aqueous solutions at various temperatures have been reported by Van Wyk,[35] Brickwedde,[36] Clark,[37] van Emster,[38] Markham,[39] and Smith.[40] Tables 1 and 2 include most of the results.

Freezing point data were determined and plotted versus composition by Van Wyk[35,41] and by Brickwedde[36] to identify hydrates.

Vapor pressures and activity coefficients were measured by Pearce and Nelson,[42] Robinson and Baker,[43] and Robinson and Stockes.[44] Results are compiled in Tables 3 and 4. Boiling points of various aqueous compositions are listed in Table 5.

Viscosities are reported by Brickwedde,[36] Van Wyk,[35] Clark,[37] and Simon.[45] Table 6 includes the data.

Surface tension data of Neros and Eversole,[46] given in Table 7, indicate that a maximum occurs at a composition corresponding to $HClO_4 \cdot 3H_2O$.

Refractive index measurements are reported by McLean and Pearson[47] for perchloric acid solutions of 0 to 72 per cent concentration at 20° and 30°. Their data are compiled in Table 8 and provide a convenient means of determining concentration of aqueous perchloric acid solutions. A plot of molar refraction against acid concentration yields a smooth curve with a minimum at 18% $HClO_4$.[48-49] From density and refractive index data, a radius for the perchlorate ion of 1.82 Å[51] and apparent molal volumes[48-50] were calculated.

Electrical resistivity and conductance measurements have been reported by Brickwedde[36] of solutions 10 to 70 weight per cent perchloric acid from —60 to +50° C, by Usanovich and Sumarokova[52] for 0 to 100% $HClO_4$ at 50°, and by Klochko and Kurbanov.[53] Discontinuities in the specific conductance curves corresponding to tri- and tetra-hydrates and a maximum at 37 weight per cent $HClO_4$ were found[52,53]. Viscosity and electrical conductance of perchloric acid solutions from —50 to +90°C were reported recently by Maksimova et al.[54] Conductance, transport numbers, diffusion coeffients, and related quantities have been reported for aqueous perchloric acid at 25° C by Haase.[55]

TABLE 1. DENSITIES OF AQUEOUS PERCHLORIC ACID SOLUTIONS[36]

HClO₄ Wt. %	Density (g/ml) at Various Temperatures (°C)							
	40°	30°	25°	20°	10°	0°	—10°	—20°
0	0.992	0.996	0.997	0.998	1.000	1.000	....	....
5	1.020	1.024	1.026	1.027	1.029	1.031	....	....
10	1.050	1.054	1.056	1.058	1.061	1.064	....	....
15	1.081	1.086	1.088	1.091	1.095	1.099	1.102	....
20	1.114	1.120	1.123	1.125	1.131	1.136	1.140	....
25	1.150	1.157	1.160	1.163	1.169	1.175	1.180	....
30	1.189	1.196	1.200	1.204	1.210	1.217	1.223	1.228
35	1.232	1.239	1.244	1.247	1.255	1.262	1.268	1.275
40	1.278	1.286	1.291	1.294	1.303	1.311	1.318	1.326
45	1.329	1.338	1.343	1.347	1.356	1.366	1.375	1.384
50	1.385	1.395	1.400	1.405	1.415	1.425	1.436	1.447
55	1.445	1.456	1.462	1.467	1.478	1.490	1.502	1.514
60	1.510	1.521	1.527	1.533	1.545	1.558	1.571	1.584
65	1.578	1.590	1.596	1.603	1.616	1.629	1.643	1.656
70	1.645	1.658	1.664	1.672	1.685	1.699	1.712	1.725

TABLE 2. SPECIFIC GRAVITY OF PERCHLORIC ACID SOLUTIONS[35]

HClO$_4$ Mole %	HClO$_4$ Weight %	Specific Gravity 20°C	Specific Gravity 50°C
100	100	1.7676	1.7098
92.75	98.62	1.7817	1.7259
76.15	94.69	1.8059	1.7531
63.85	90.78	. . . . .	1.7690
50.00	84.80	. . . . .	1.7756
43.4	81.06	. . . . .	1.7619
35.67	75.57	1.7386	1.7023
27.96	68.41	1.6471	1.6110
21.44	60.37	1.5353	1.5007
15.46	50.50	1.4078	1.3779
10.56	39.72	1.2901	1.2649
6.23	27.05	1.1778	1.1574

TABLE 3. VAPOR PRESSURE OF PERCHLORIC ACID AQUEOUS SOLUTIONS AT 25°C[42]

Molality HClO$_4$	Vapor Pressure, mm
0.0	23.752
0.20064	23.593
0.60655	23.254
1.01589	22.870
3.1512	20.192
5.4347	16.308
7.8719	11.490
10.5139	6.838

TABLE 4. MEAN ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS OF AQUEOUS PERCHLORIC ACID SOLUTIONS AT 25 °C[43]

$HClO_4$ Molarity	Activity Coefficient $f\pm$	Osmotic Coefficient f_0
0.2	0.766	0.951
0.4	0.754	0.966
0.6	0.763	0.988
0.8	0.784	1.013
1.0	0.810	1.041
2.0	1.039	1.210
3.0	1.420	1.406
4.0	2.018	1.622
5.0	2.94	1.860
6.0	4.41	2.106
7.0	6.90	..
8.0	11.32	..
9.0	18.0	..
10.0	29.0	..
11.0	47.3	..
12.0	77.7	..

TABLE 5. COMPOSITION OF LIQUID AND VAPOR PHASES OF AQUEOUS PERCHLORIC ACID AT DIFFERENT BOILING POINTS

Boiling point °C	Pressure mm	Weight per Cent $HClO_4$ Liquid	Weight per Cent $HClO_4$ Vapor
203	760	72.40	72.40
198.7	760	70.06	40.11
181.2	760	65.20	6.06
162.3	760	61.2	0.90
148.0	760	56.65	..
114.8	760	38.90	..
107	18	70.5	..
92	18	79.8	..
70	18	84.8	..
35	18	92.0	..
24.8	18	94.8	..
16.0	18	100	..
39	56	100	..

TABLE 6. ABSOLUTE VISCOSITY OF AQUEOUS PERCHLORIC ACID SOLUTIONS[36]

HClO4 Wt. %	Absolute Viscosity (centipoises)* at Various Temperatures (°C)							
	40°	30°	25°	20°	10°	0°	−10°	−20°
0	0.653	0.798	0.890	1.002	1.306	1.786	2.59	....
5	0.662	0.803	0.894	1.004	1.287	1.743	2.47	....
10	0.675	0.813	0.901	1.010	1.280	1.714	2.40	....
15	0.692	0.829	0.913	1.022	1.286	1.701	2.347	....
20	0.715	0.853	0.937	1.043	1.307	1.707	2.329	....
25	0.750	0.890	0.974	1.080	1.347	1.745	2.353	....
30	0.794	0.940	1.031	1.139	1.413	1.815	2.434	3.415
35	0.859	1.013	1.108	1.223	1.514	1.925	2.572	3.581
40	0.950	1.118	1.224	1.345	1.670	2.113	2.814	3.928
45	1.080	1.274	1.395	1.534	1.900	2.426	3.244	4.582
50	1.271	1.507	1.650	1.821	2.268	2.914	3.962	....
55	1.548	1.837	2.022	2.237	2.819	3.677	5.104	7.570
60	1.928	2.296	2.532	2.813	3.560	4.713	6.700	9.962
65	2.440	2.913	3.211	3.560	4.523	5.969	8.40	12.37
70	3.094	3.692	4.060	4.504	5.675	7.333	9.92	14.19

*Based upon absolute viscosity of water at 20°C=1.002 centipoises.

18

TABLE 7. SURFACE TENSION OF PERCHLORIC ACID SOLUTIONS[46]

HClO4 Weight %	Surface Tension at Various Temperatures (°C)		
	15°	25°	50°
0.00	73.51	71.97	68.16
4.86	72.52	71.18	67.60
10.01	71.66	70.34	66.97
20.38	70.46	69.21	66.12
30.36	69.82	68.57	65.66
40.37	69.72	68.49	65.74
53.74	70.33	69.02	66.60
60.70	70.88	69.69	67.40
63.47	70.77	69.73	67.44
67.59	70.67	69.71	67.41
70.43	70.07	69.54	67.26
72.25	69.96	69.01	66.85

19

TABLE 8. REFRACTIVE INDEX OF AQUEOUS PERCHLORIC ACID[47]

HClO₄ Weight %	Refractive Index	
	20°C	30°C
0.00	1.3330	1.3320
9.73	1.3395	1.3381
20.05	1.3470	1.3452
30.75	1.3580	1.3559
40.31	1.3680	1.3665
50.28	1.3813	1.3800
60.08	1.3983	1.3960
62.81	1.4034	1.4010
64.00	1.4054	1.4028
68.52	1.4129	1.4103
70.06	1.4151	1.4130
72.62	1.4190	1.4159

Raman spectra[56,57] and proton magnetic resonance spectra[58] have been recorded to study the degree of dissociation of perchloric acid in aqueous solutions.

Apparent molal expansibility, volume, and compressibility of aqueous solutions of perchloric acid at 25° were determined recently[59] to study their dependence on composition and the nature of anion interactions with water.

Chemical Properties

The chemistry of perchloric acid in aqueous solutions can be characterized briefly as that of an exceptionally strong acid with essentially no oxidizing strength except towards active metals that normally displace hydrogen from acids. However, if the perchloric acid be both hot and concentrated its oxidizing properties are considerable, and in certain cases dangerously vigorous. It is also a strong dehydrating agent when hot and concentrated. Under such conditions it serves as an highly efficient oxidant for destruction of organic matter. When dilute or cold, however, its oxidizing strength is so greatly diminished that it is suitable for use without interference in the study of many redox reactions. Likewise, the very weak tendency for perchlorate ions to coordinate to metal ions favors the use of perchloric acid as a non-interfering acid in complexation studies.

Perchloric acid is one of the strongest acids known. Its effective strength depends, like any other acid, on the basicity of the solvent in which it is dissolved. In water it is completely ionized in the most concentrated solutions and completely dissociated up to a concentration of about 4 M, where the first appearance of undissociated HClO₄ has been detected.[60] In concentrated sulfuric acid it is strongly dissociated but weaker than disulfuric acid ($H_2S_2O_7$).[61] In organic solvents it behaves as a strong acid, highly ionized but not necessarily highly dissociated, depending on dielectric and solvation strengths of the solvent. As a strong acid it is especially useful in measuring pK values and relative strengths of very weak bases. Hammett acidity functions for this purpose have been measured by various workers, including Gillespie,[62] Yates et al.,[63,64] and Attiga and Rochester.[65] Values of the acidity function, H_0, for perchloric acid in acetic

acid-water mixtures have been determined by Wiberg and Evans.[66]

Certain strong reductants are oxidized by perchloric acid at room temperature. Increasing the concentration of perchloric acid favors its reaction rate as an oxidant, suggesting that the protonated form rather than the perchlorate ion is the active species.[67] Some of the reductants investigated in reaction rate studies include ruthenium(II),[68] titanium(III),[69] molybdenum(III),[70] chromium(II),[70] titanous chloride or sulfate,[17] platinum cathode,[72] hydrogen and simple organic fuels,[73] and various metals.[74] Reductants for perchlorates are further discussed in Chapter VII.

Perchloric acid solutions are decomposable thermally or by exposure to ionizing radiation. Studies of its thermal decomposition indicate an activation energy for decomposition of 22.56 kcal/mol[75], an autocatalytic effect for 65-100 wt % $HClO_4$,[76] and heterogeneous catalysis by oxides of iron, copper or chromium.[77] Radiolysis studies reveal that perchloric acid decomposes only as a result of direct action of the radiation, yielding chlorate ions as major product, and that it does not react with products from the radiolysis of water.[78-80]

HYDRATES OF PERCHLORIC ACID

A total of five different hydrate compositions have been identified from studies of liquid-solid equilibriums in the binary system perchloric acid-water. Several different investigators confirm these findings. Van Wyk,[35,41] the first to investigate the system, found the following hydrates: $HClO_4 \cdot H_2O$, $HClO_4 \cdot 2H_2O$,, $HClO_4 \cdot 2.5H_2O$, α- and β-forms of $HClO_4 \cdot 3H_2O$, and $HClO_4 \cdot 3.5H_2O$. Brickwedde[36] obtained a freezing point-composition plot very similar to that of Van Wyk's but with different, presumably more accurate, temperatures. Zinov'ev and Babaeva[81] confirmed the existence of all five hydrates, noting also that the mono- and dihydrate exist in aqueous solution up to a temperature of 75° and that the other three hydrates are much more highly dissociated. Mascherpa and coworkers,[82] on repeating the study of Van Wyk over the concentration range of 58-74 wt. per cent $HClO_4$, found hydrates of 1 molecule of $HClO_4$ with 2, 2.5, 3, and 3.5 molecules of H_2O, exhibiting melting points re-

spectively of —20.65°, —32.1°, —40.2°, and —45.6° (all ± 0.1°). A sixth hydrate composition, corresponding to $H_2O \cdot 4HClO_4$, has been reported by Mascherpa,[84] based upon a thermal analysis study.

Perchloric acid hydrates involve considerable hydrogen bonding. A bond-valence analysis of five of the hydrates by Brown[84] shows that normal H-bonds account for only about one-half of the bonding of the perchlorate ion. Each H-atom also forms an average of four additional weak interactions. The infrared spectrum of crystalline perchloric acid trihydrate is consistent with H_3O^+ central pattern complexed by two water molecules through short asymmetric hydrogen bonds.[85] Perchlorate ions participate to some extent in hydrogen bonding in the hydrate $HClO_4 \cdot 3.5 H_2O$ according to Almlof.[86] For this hydrate, X-ray diffraction data[86] at —188° indicates two independent $H_9O_4^+$ complexes having one water molecule in common. The two perchlorate ions show only minor deviations from tetrahedral symmetry, with mean Cl-O distances of 1.437 and 1.443 Å.

The most extensively studied hydrate is the monohydrate. It exists entirely as the oxonium salt $H_3O^+ClO_4$ and thus can be correctly referred to as oxonium perchlorate. It contains 84.78 per cent $HClO_4$ by weight, forms long needle-like crystals, melts at 49.905° with considerable expansion, and exhibits a heat of fusion of 2.46 ± 0.08 kcal/mole. Methods for its preparation, described by Roscoe[87] and by Klages,[88] involve preparation of the anhydrous acid and treatment with an appropriate amount of either water or perchloric acid dihydrate. Oxonium perchlorate dihydrate can be safely stored at room temperature indefinitely without decomposition if protected from reactive substances.

The crystal structure of oxonium perchlorate has been determined by X-ray diffraction.[89] A reversible phase change occurs —23.4° accompanied by an increase in density.[90] Below this temperature, at —80° Nordman[91] reports that the crystal structure belongs to the monoclinic space group and consists of H-bonded layers of perchlorate and hydronium ions. Above the transition point the structure is orthorhombic and more disordered. The perchlorate ions are nearly perfect tetrahedra with an average Cl-O distance of 1.42 Å. Proton magnetic resonace spectra[92] indicate that the oxonium

ion has a pyramidal structure. The Raman spectrum[93] is consistent with the X-ray and NMR findings, and valence force constants have been calculated.

Dioxonium perchlorate (perchloric acid dihydrate, 73.60 wt. % $HClO_4$) boils at 203° at atmospheric pressure, is hygroscopic, fumes in moist air, and freezes at —17.8°. Recommended as a primary standard for acidimetry,[40] it can be prepared by distilling 70-72% $HClO_4$ at 2-7 mm and discarding the first-half or more of the distillate before collecting the dioxonium perchlorate.

ANHYDROUS PERCHLORIC ACID

Preparation and Properties

The preparation of anhydrous perchloric acid can be readily achieved by fractional distillation of a mixture of concentrated sulfuric acid and 65-70% perchloric acid.[94,95] Magnesium perchlorate,[96] phosphorous pentoxide,[97] and sulfur trioxide[97] have also been described as dehydration agents in place of sulfuric acid. Anhydrous perchloric acid can also be obtained by extration into methylene chloride from a mixture of one part by volume of 70% perchloric acid and four parts 25% fuming sulfuric acid.[88] It has been recommended that only small amounts of reagents be used in this procedure and that the extraction flask be kept cold because of the risk of an explosion.[98] Procedures for the preparation of anydrous deuterium perchlorate and D_3OClO_4 have been described by Smith and Diehl.[99]

The anhydrous acid is colorless, hygroscopic, volatile, extremely reactive, and explosively unstable. In contact with skin it produces serious and painful wounds. On addition to water it generates considerable heat and a hissing noise. It freezes at —112° and boils at 18 mm at 16° without decomposition. It can not be distilled at ordinary pressures without decomposition and explodes at about 90°. On standing at ordinary temperatures the pure acid gradually yellows and eventually (within 10 to 30 days) explodes spontaneously. Storage time can be extended up to 60 days by use of liquid-air temperatures without formation of colored decomposition products. Extreme caution is necessary to avoid contacting the anhydrous acid with wood, paper, or other combustible matter because explosions invariably result, even at ordinary temperatures. Except for special use or need anhydrous perchloric acid should not be made or stored.

Anhydrous perchloric acid undergoes partial autodissociation to chlorine heptoxide and oxonium perchlorate above its melting point, and the rate of attainment of equilibrium increases rapidly above —30°.[100] The existence of the equilibrium $3 HClO_4 \rightleftharpoons Cl_2O_7 + HClO_4 \cdot H_2O$ has been demonstrated from viscosity,[101] kinetics of decomposition and vapor pressure,[102] and electrical measurements.[103] Rosolovskii[102] reports values for the equilibrium constant (as written above) of 0.80×10^{-4} at —10°, 1.30×10^{-4} at 20°, and 1.94×10^{-4} at 70°. Bout and Potier[103] report a value of 0.60×10^{-6} for the self-dissociation equilibrium constant of the following reaction:

$$3 HClO_4 \rightleftharpoons ClO_2O_7 + H_3O^+ + ClO_4^-$$
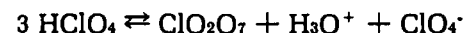
This value differs from Rosolovskii's because of the difference in formulating the oxonium perchlorate product. The extent of self-dissociation is thus indicated in either formulation at approximately 1 per cent.

Heat capacities and thermodynamic functions for anhydrous perchloric acid from 5 to 55°K indicate that $HClO_4$ exists as an independent species in the crystalline state.[104] At 298.15 °K its heat capacity, C_P, is 28.80 cal/mol degree. A triple point occurs at 172.0 °K.

Raman and infrared spectra of anhydrous $HClO_4$ and $DClO_4$ have been extensively studied for all three physical states.[105-7] There is no evidence of any molecular association in the liquid state. Bond energies, bond lengths, and standard thermodynamic quantities have been estimated from the data.[105]

The thermal decomposition of anhydrous perchloric acid has been studied extensively.[108-116] Proceeding through the formation of Cl_2O_7, the following decomposition products are formed at 60-80°; O_2, $HClO_4 \cdot H_2O$, ClO_2, and Cl_2.[111] At 200-439° the products are Cl_2, H_2O, and O_2.[110] In addition to Cl_2O_7, other probable intermediates include ClO_3 and ClO_4. At 10 mm and 300-400°, the decomposition is first order with respect to $HClO_4$. Catalysts, in order of their activity, are $Co_2O_3 > MnO_2 > CuO > Fe_2O_3 > CuCr_2O_4 > Al_2O_3 > SiO_2$.[116]

Reactions

An extremely powerful oxidant, anhydrous perchloric acid causes explosions upon contact with most organic substances. It can, however, be dissolved in chloroform, methylene chloride, acetic acid, and certain other organic solvents for somewhat safer employment in chemical reactions and syntheses. On dissolving it in acetonitrile, it interacts with the solvent by H-bonding initially and then very slowly transfers its proton to the acetonitrile.[117] Applications of the anhydrous acid in various organic solvents have been reviewed by Burton and Praill.[118]

Neither hydrogen chloride nor hydrogen bromide react with anhydrous perchloric acid but hydrogen iodide as well as sodium iodide ignite on contact with it. Thionyl chloride also ignites on contact but not sulfuryl chloride. Phosphorous oxychloride dissolves it without reaction, while phosphorous pentachloride reacts to give chlorine heptoxide. A solution of the acid in chloroform explodes violently if poured upon phosphorous pentoxide. Reaction with iodine yields deliquescent needles of $HIO_3(I_2)_3$, which when warmed give off iodine and leave iodic acid as a residue.

Graphite reacts slowly with the anhydrous acid at room temperature to give $C_{24.9}ClO_4$ and ClO_3.[119] However, a drop added to wood charcoal produces a violent explosion. Paper and wood are ignited by the acid. The gas-phase reaction of perchloric acid with hydrogen is first order in either reactant and yields hydrogen chloride.[120] Methane or ammonia is without effect on the gas-phase reaction with hydrogen.[121] In the gas-phase reaction of perchloric acid with ethylene the major products are HCl, CO, and H_2O; some 1,2-dichloroethane and vinyl chloride is also produced together with minor amounts of numerous other organic compounds, including C_3 and C_4 halides.[122]

PERCHLORIC ANHYDRIDE

Chlorine heptoxide, the anhydride of perchloric acid, was first isolated by Michael and Conn[30] by adding anhydrous perchloric acid very slowly to phosphorous pentoxide cooled to —10°, and after one day at —10°, distilling the product from the mixture at 82°. They carefully reported that "the apparatus may be virtually pulverized by violent explosion, and personal precautions must be taken accordingly." More recently, Kolarov et al.[123] described a method which involves heating a mixture of anhydrous magnesium perchlorate with phosphorous pentoxide in a ratio of 1 to 1-2 at 100-160° and 1-2 mm for 2-5 hours to obtain a pale yellow-to-orange product as distillate collected in a receiver cooled to —78°. The distillate is free of phosphoric acid but contains lower oxides of chlorine. Use of hydrated magnesium perchlorate led to an explosion. Replacement of magnesium perchlorate with potassium or ammonium perchlorate gave no product.

Chlorine heptoxide. Cl_2O_7, is a colorless volatile oil which decomposes spontaneously on standing for a few days, turning greenish-yellow. According to Babaeva,[124] only 33.5% decomposed in 502 min. at 80°. In the presence of 1% $HClO_4$ the rate of oxygen evolution is increased and the final product is oxonium perchlorate.

Perchloric anhydride is soluble in and slowly attacks benzene, reacts slowly with water to form perchloric acid, reacts with iodine to form iodine pentoxide, and explodes on contact with flame or by percussion. It volatilizes rapidly, so that a small amount dropped onto paper or wood may evaporate before it can react violently. Reaction with olefins yields impact-sensitive alykl perchlorates.[125] It is soluble in phosphorous oxychloride, producing normal freezing point lowering indicative of the molecular state Cl_2O_7.[126]

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CHAPTER III

PROPERTIES AND PREPARATION OF PERCHLORATES

REPRESENTATIVE (SUB GROUP A) METAL PERCHLORATES

Ammonium and Alkali Metal Perchlorate

The anhydrous salts of the alkali metal perchlorates are isomorphous with one another and with ammonium, thallium, and silver perchlorates. Their crystal structures have been determined by X-ray and optical methods.[1] With the exception of lithium perchlorate, all exhibit dimorphism undergoing transitions from rhombic to cubic forms at characteristic temperatures.[2-4] Their structural transformations have also been examined by differential thermal analysis.[5-6]

Thermochemical data for various aqueous solutions of the ammonium and alkali metal perchlorates, heats of solution, heats of formation, and thermochemical data for the anhydrous salts have been determined by numerous investigations.[7-12] Solubilities of the perchlorates in various solvents were determined by Willard and Smith.[13] Magnetic susceptibilities[14] and molar refractions[15] have also been determined. Many of the results of these various determinations are compiled in Table 9.

Additional thermochemical data, not included in Table 9 nor in complete agreement with previous data, have been reported recently. Birky and Hepler report heats of solution at 25° for lithium, ammonium and potassium perchlorates of —6.31, 8.02, and 12.31 kcal/mole, respectively.[16] Vorob'ev et al. report that the enthalpies of formation of sodium and potassium perchlorates are —90.68 and —101.9 kcal/mole, respectively.[17]

Guenther[18] found that the solubilities of rubidium and cesium perchlorates in the presence of univalent strong electrolytes (ionic strengths 0.068 to 0.46 M) are accurately predicted by simple Debye-Huckel theory. Values obtained for the pKsp (—log of the solubility product) of potassium, rubidium, and cesium perchlorates at 25° are 1.944, 2.542, and 2.380, respectively.

TABLE 9. PHYSICAL PROPERTIES OF AMMONIUM AND ALKALI METAL PERCHLORATES AT 25°C

Physical Property	Magnitude of Physical Property of Perchlorate					
	NH4	Li	Na	K	Rb	Cs
Density	1.952	2.429	2.499	2.5298	2.9	3.327
Solubility (g/100g solv.)						
Water	24.922	59.71	209.6	2.062	1.338	2.000
Methanol	6.862	182.25	51.36	0.105	0.060	0.093
Ethanol	1.907	151.76	14.71	0.012	0.009	0.011
n-Propanol	0.387	105.00	4.888	0.010	0.006	0.006
Acetone	2.260	136.52	51.745	0.155	0.095	0.150
Ethyl Acetate	0.032	95.12	9.649	0.001	0.016	0.000
Ethyl Ether	0.000	113.72	0.000	0.000	0.000	0.000
Thermochemical data						
ΔH_f°, kcal/mole	—69.42	—91.77	—92.18	—103.6	—103.9	—103.9
ΔF_f°, kcal/mole	...	...	...	—72.7	—73.2	—73.3
ΔS_f°, kcal/mole	...	...	...	36.1	38.4	41.9
C_p°, kcal/mole	...	...	...	26.33	...	25.71
Molar heat of solution	6.36	6.24	3.51	12.1	13.6	13.3
Magnetic subsceptibility (x10^6)	46.3	32.8	37.6	47.4	...	69.9
Molar refraction	17.22	...	13.58	15.37	...	...

Rosolovskii and coworkers[19] report that the solubility of the perchlorates in anhydrous perchloric acid at 0° depends on the radius of the cation but not its nature. The following solubilities (in g of solute per 100 g. $HClO_4$ were found: 0.106 $LiClO_4$, 0.628 $NaClO_4$, 4.256 $KClO_4$, 22.56 $RbClO_4$, and 68.40 $CsClO_4$.

Thermal decomposition and differential thermal analysis studies of the crystalline solids have been carried out by various investigators.[5,6,20-22] Lithium, sodium, and potassium perchlorates yield oxygen and the respective chloride on thermolysis.[20] Gas evolution measurements and DTA[22] indicate that lithium perchlorate melts at 241°, decomposes at 489°, and does not undergo a phase change. By similar means potassium and sodium perchlorates were found to undergo endothermic phase change at 306° and 304°, melt at 575° and 468°, and decompose at 620° and 561°, respectively.[22]

Alkali metal perchlorate solutions have been studied extensively to gain information about the perchlorate ion. From electrical conductance measurements, Jones[23] found a value of 67.32 ± 0.06 mhos for the limiting equivalent conductance of the perchlorate ion. The standard enthalpy of formation of the perchlorate ion in infinitely dilute aqueous solution is —30.87 ± 0.07 kcal/g, according to Kirpichev.[24] The crystal radius of the perchlorate ion is 1.85 Å, determined from results of solvation studies of alkali metal perchlorates.[25] Calculations based on Raman and infrared spectra of aqueous solutions indicate a hydration number of four for perchlorate ions.[26] The tendency for perchlorate ions to form contact ion pairs was studied as a function of cation and solvent by chlorine-35 nuclear magnetic resonance.[27] Factors favoring contact ion pairing are high charge to radius ratio of cation, low dielectric constant of solvent, and low basic strength of solvent. The possibility of perchlorate ion coordination to various metal ions and other species has been explored by vibrational spectroscopy and other techniques and will be discussed in a later section with transition metal perchlorates.

A convenient general preparation method for any alkali metal perchlorate consists of the treatment of the hydroxide, oxide, or metal with perchloric acid followed by isolation of the neutral salt by crystallization. Sodium and potassium perchlorates can be obtained by treating their chlorides or fluorides with nitrosyl perchlorate, $NOClO_4$.[28] Commercial quantities of sodium perchlorate are best prepared by electrolysis of aqueous solutions of sodium chloride.[29,30] Commercial quantities of ammonium, lithium, potassium, rubidium, and cesium are best prepared from sodium perchlorate by metathesis (double-decomposition) reactions, taking advantage of the much higher aqueous solubility of the sodium perchlorate than the other perchlorates in order to fractionally crystallize the desired perchlorate.[29]

Ammonium Perchlorate. The anhydrous salt is prepared by reaction of sodium perchlorate with ammonium sulfate or chloride. No hydrates are known but a triammine with a dissociation pressure of 2 mm at —79° has been reported.[31] Its solubility in ammoniacal solutions increases slightly with increasing ammonia concentration.[32] In aqueous perchloric acid solutions its solubility decreases with increase of perchloric acid concentration and increases with increasing temperature.[33] Densities of aqueous solutions of ammonium perchlorate at 15° and 25° have been determined.[34] An increase in volume results at 25° when ammonium perchlorate is dissolved in water, but a decrease occurs at 15°.

Thermal decomposition of ammonium perchlorate has been studied extensively because of its effectiveness as an oxidant in rocket propellants and as an explosive. It is stable at 110°, decomposes at 130°, and explodes at 380°.[35] Below 300° the decomposition reaction is described by the following equation:[35-38]

$$4\ NH_4ClO_4 \rightarrow 2\ Cl_2 + 8\ H_2O + 2\ N_2O + 3\ O_2$$

Above 400° most of the nitrogen is evolved as nitric oxide.[35] The activation energy for decomposition changes from 18.9 to 29.6 kcal/mole on increasing the temperature above 240°, a change that coincides with the crystal transition from orthorhombic to cubic at 240°. From 400° to 440°, under nitrogen pressure of 20 torr to control sublimation, the decomposition of ammonium perchlorate exhibits an activation energy of 23.4 kcal/mole and probably involves decomposition of the vapor rather than solid phase.[38]

A differential thermal analysis study of the ammonium perchlorate-lithium perchlorate has been reported, indicating

a simple eutectic exists at 182° and 69.5 mole % $LiClO_4$.[39] Studies of ternary and quarternary systems involving ammonium perchlorate are cited in the Appendix.

Lithium Perchlorate. The trihydrate is obtained by crystallization from a mixture of lithium carbonate and 70% perchloric acid,[40] or by electrolysis of a solution of lithium chlorate.[41] Conversion of the trihydrate to anhydrous lithium perchlorate, with a molar heat of hydration of 14.2 kcal to overcome, requires prolonged drying at 300°.[40] Pruntsev and coworkers have patented a process for obtaining anhydrous lithium perchlorate by heat treatment at 170-200°.[42]

In addition to forming a very stable hydrate, lithium perchlorate forms a di-, tri-, and pentammine, exhibiting dissociation pressures of 2 mm at 20°, 39.5 mm at 20°, and 31 mm at —79°, respectively.[31]

Lithium perchlorate is thermally stable at and above its melting point at 247°, according to Markowitz.[4] Thermal decomposition, yielding oxygen and lithium chloride, occurs at an appreciable rate at 400° and is catalyzed by the chloride product.[43,44] The autocatalysis is affected by addition of silver nitrate in the lithium perchlorate melt.[44-45]

The solubility of lithium perchlorate in water and the densities of the saturated solutions between 0° and 40° have been determined,[46] also the densities of non-saturated aqueous solutions at 15°.[47] Solubilities in acetone and in methyl ethyl ketone have been reported for the —50° to +50° range.[48]

The structure of lithium perchlorate trihydrate has been determined in detail by an X-ray and neutron diffraction study,[49] and its hydrate water structure has been examined by proton magnetic resonance.[50] The lithium atoms are coordinated by an almost regular octahedron of water molecules (2.133 Å average Li-O bond distance), the perchlorate ions have a regular tetrahedral structure (1.440 Å Cl-O bond distance), and each hydrogen atom forms a weak bond (2.044 Å) with one perchlorate-oxygen atom and a very weak bond (2.617 Å) with a second perchlorate-oxygen atom.

Sodium Perchlorate. Electrochemical oxidation of aqueous sodium chloride solutions is the most common method for preparing sodium perchlorate. Many different studies,

electrodes, and procedures have been described over the years. Improvements recently reported include use of lead dioxide on carbon or titanium as efficient anode materials,[51,52] decreased temperatures,[53,54] and addition of sodium fluoride.[55] For the anodic oxidation of sodium chlorate to sodium perchlorate, increased current efficiency is claimed if potassium persulfate is added.[56] Another approach uses a lead dioxide anode for chlorate concentrations of 250-300 g/l and then changes to a platinum anode when the chlorate concentration has been depleted by electrolysis to one-half its original value.[57]

Sodium perchlorate forms a monohydrate, with a heat of hydration of 2.01 kcal/mole, which can be completely dehydrated at 130°. The anhydrous salt is stable to temperatures up to 471° before loss of oxygen and formation of sodium chloride occurs.[58] Sodium perchlorate also forms a tetrammine.[31]

The solubility of sodium perchlorate in aqueous solutions,[59] perchloric acid solutions,[59] and in water-dimethyl sulfoxide media[60] has been studied. Conductivity of the salt has been measured in water,[61] methanol,[62] ethanol,[63] dimethylformamide,[64] nitromethane,[65] hydrocyanic acid,[66] and hydrazine.[67]

A detailed crystal structure of sodium perchlorate monohydrate has been determined by Berglund and coworkers,[68] who subsequently performed a neutron diffraction study[69] and a deuteron magnetic resonance study of the solid.[70] A chlorine-35 NMR relaxation study of aqueous sodium perchlorate solutions has also been reported.[71]

Studies of ternary and quaternary systems involving sodium perchlorate are cited in the Appendix.

Potassium Perchlorate. The thermal decomposition of potassium perchlorate is complex and has been extensively studied because of the interest in its use as an oxidizer in solid rocket propellants. Decomposition of the pure salt has been detected at a temperature as low as 530°,[72] although others found it to be stable at higher temperatures.[58,73] The kinetics of its isothermal decomposition[74] under constant oxygen pressure[75] and under its own evolved oxygen pressure[76] have been investigated.

No hydrates or ammoniates have been reported for potassium perchlorate. Solubility data up to a temperature of 265° have been determined.[77] Activity coefficients, determined from solubilities in various salt solutions, have been reported.[78] Conductivities in hydrazine,[67] hydrogen cyanide,[68] and dimethylformamide[84] have been measured.

Alkaline Earth Perchlorates

Anhydrous perchlorates of the alkaline earth metals can be prepared by heating ammonium perchlorate with the corresponding oxides or carbonates.[79] They can also be prepared by heating their hydrates with pyridine, eventually driving off pyridine without decomposition of the perchlorate.[80] The hydrates are prepared by treatment of the metal oxides or various salts with aqueous perchloric acid.[13]

All of the alkaline earth perchlorates form hydrates, amines, and pyridine adducts. The hydrates are identified in Table 10 with data reported for their heats of hydration.[8,81] The amines correspond to M(ClO₄)₂ · nNH₃, where n = 2, 6, and 7 for Mg; 2, 3, 4, 6 and 7 for Ca; 1, 2, 6, 7, 10 and 12 for Sr; and 2, 5, 6 and 9 for Ba.[82-84] The pyridine complexes correspond to M(ClO₄)₂ · n(C₆H₅N), where n = 2 and 4 for Be; 1, 2, 4 and 6 for Mg; 1 and 2 for Ca and Sr.[80,85] Their thermal stability increases with decreasing number of pyridine groups.

The basic salts M(OH)ClO₄ (where M is Mg, Ca, or Ba) have been prepared and characterized.[86]

Alkaline earth perchlorates are unusually soluble in organic solvents, as evidenced by the data of Willard and Smith[13] compiled in Table 10. Curiously, calcium and barium perchlorates are more soluble in methanol than in water. The solubilities of magnesium, strontium, and calcium perchlorates in water have been measured for the 0° to 50° range.[87] Magnetic susceptibilities[14] and apparent molar volumes,[88] the latter deduced from density measurements of aqueous solutions, are given in Table 10. Vapor pressure[89] and density measurements[90] have also been reported for aqueous solutions of the metal perchlorates at various temperatures.

Beryllium Perchlorate. The dihydrate has been prepared by heating a mixture of beryllium chloride and oxonium perchlorate to 60° in vacuum.[91] Infrared spectra re-

TABLE 10. PHYSICAL PROPERTIES OF ALKALINE EARTH PERCHLORATES AT 25°C

| Physical Property | Magnitude of Physical Property of Perchlorate | | | |
	Mg	Ca	Sr	Ba
Solubility (g/100 g Solvent)				
Water	99.601	188.60	309.67	198.33
Methanol	51.838	237.38	212.01	217.06
Ethanol	23.962	166.24	180.66	124.62
n-Propanol	73.400	144.92	140.38	75.65
Acetone	42.888	61.860	150.06	124.67
Ethyl Acetate	70.911	75.623	136.93	112.95
Ethyl Ether	0.291	0.261	0.000	0.000
Heat of formation, ΔH_f°, kcal/mole	—140.6	—178 (est.)	—184 (est.)	—192.8
Heat of hydration, kcal/mole				
Dihydrate	13.509	......	9.5	......
Trihydrate	......	......	......	8.63
Tetrahydrate	24.724	15.485	13.2	......
Hexahydrate	32.708	......	......	......
Apparent molar volume, cm³/mole	63.2	69.0	71.5	76.3
Magnetic suceptibility (x10⁶)	65.0	70.5	81.4	94.7
Density of saturated aqueous solution	1.4720	1.7191	2.0837	1.9403

vealed that the product contains $Be(H_2O)_4^{+2}$ and $Be(ClO_4)_4^{-2}$ ions. It melts below 80°, forms an oxo- or hydroxy-containing compound at 150°, loses $HClO_4$ and forms a solid residue $Be_4O(ClO_4)_6$ in the temperature range 190° to 165°, and eventually yields beryllium oxide on further heating to 290°. The tetrahydrate, when heated in an atmosphere of helium, decomposes in the liquid phase to form $Be(OH)(ClO_4)$ which then decomposes to beryllium oxide and anhydrous perchloric acid.[92] Novoselova and coworkers have prepared cesium, rubidium, and potassium perchloratoberyllates of general formula $M_2Be(ClO_4)_4$ and interpreted their infrared spectra obtained as Nujol mulls in the 200-4000 cm^{-1} region.[93]

Magnesium Perchlorate. The anhydrous salt serves as an extremely efficient drying agent.[94] It also strongly absorbs ammonia, ether,[95] and many other polar organic vapors.[96] Vapor pressure measurements have been made of the water-magnesium perchlorate system, indicating the existence of a di-, tetra- and hexahydrate, but no trihydrate.[97]

A thermogravimetric study indicated a gradual weight loss with no sharp break in the temperature-weight curve for magnesium perchlorate hexahydrate decomposing to magnesium oxide.[98] Another study identified $(MgCl)_2O$ as the final product of the thermal decomposition.[99] Markowitz[100] reports that a mixture of magnesium oxide and chloride is formed. A kinetic study by Novoselova and coworkers[101] indicates that magnesium perchlorate undergoes two-stage decomposition: first to $MgO \cdot Mg(ClO_4)_2$, and subsequently to either MgO and $Mg(ClO_4)_2$ (below 165°) or MgO, Cl_2 and O_2 (above 165°).

Conductances have been measured for solutions of magnesium perchlorate in water[102] and various nonaqueous solvents.[103-105] Osmotic and activity coefficients have been reported.[106] The structure of magnesium perchlorate has been investigated by X-ray[107] and Raman[108] techniques.

Calcium Perchlorate. Studies reported for calcium perchlorate include conductivity in acetone,[104] adiabatic compressibility of aqueous solutions,[109] enthalpies of dilution and relative apparent molar enthalpy of aqueous solution,[110] and kinetics of thermal decomposition.[111]

Strontium Perchlorate. Conductances in methanol-acetone solutions[105] and adiabatic compressibility[109] of aqueous solutions of strontium perchlorate have been measured.

Barium Perchlorate. Preparation and use as drying agents of the anhydrous salt[94] and of the trihydrate[112] have been described by Smith. The ammoniates and their equilibrium dissociation pressures have been reported by Smeets.[113] The conductance of barium perchlorate in several different organic solvents has been measured.[114] Vibrational spectra of the crystalline trihydrate have been analyzed,[115] indicating insufficient lattice dissymmetry for a measurable piezoelectric effect or optical activity.

Groups IIIA - VA Metal Perchlorates

Although the perchlorates of all of the representative metals have been prepared, those of Groups III to V of the periodic table have not been studied as thoroughly or as systematically as those of Groups I and II. Perhaps the most distinctive features of metal perchlorates as a class are their relatively large solubilities in organic solvents, their appreciable affinities for water and hydrate formation, and their proclivities to undergo thermal decomposition and sometimes explosions. Most of the literature published on each compound is cited or briefly summarized below.

Aluminum Perchlorate. In addition to the anhydrous salt, five different hydrates have been described with 3, 6, 9, 12 and 15 moles of water.[1] All except the 15-hydrate are hygroscopic. The 9-hydrate has a very high water solubility, 462.75 g per 100 g of water at 0°. Existence of the 12-hydrate has yet to be confirmed. Anhydrous aluminum perchlorate can be prepared by drying its hydrates over phosphorous pentoxide in vacuum at 150°,[116] by treatment of anhydrous aluminum chloride with anhydrous perchloric acid,[117] or by reaction of anhydrous aluminum chloride with silver perchlorate in methanol or benzene.[118]

Viscosities, densities, electrical conductances, molar refractions, molar volumes, and compressibilities of various aqueous solutions of aluminum perchlorate have been reported.[119-122] Conductivities have also been determined in some nonaqueous solvents.[117,123] Thermal decomposition

studies have been made identifying aluminum oxide as the final product.[20,124] Vibrational spectra indicate that the anhydrous compound is covalent with bidentate perchlorate groups.[125] Raman spectra of aqueous solutions[126] and proton magnetic resonance spectra of alcoholic solutions[127] have been analyzed.

Preparation of perchloratoaluminates, with infrared spectra indicating a general structure $M[Al(ClO_4)_4(H_2O)_2]$ (where M is either cesium or rubidium), has been reported.[128] Tetraalkylammonium haloperchloratoaluminates have also been prepared.[129]

Gallium and Indium Perchlorates. Viscosities and densities of aqueous solutions of gallium and indium perchlorate have been measured over the temperature range 18° to 90°.[122] Sound velocities and densities also have been determined at 25°.[121] Gallium perchlorate is very deliquescent, highly soluble in water, forms a 6- and a 9-hydrate, and decomposes at 155° in a vacuum or at 175° exposed to air. Attempts to dehydrate the hexahydrate produced a basic salt. Isospiestic studies of aqueous solutions of gallium perchlorate have been made,[130] and activity coefficients have been measured.[131] Indium perchlorate has been little studied.

Thallium Perchlorate. The crystal structure of thallium perchlorate is isomorphous with the alkali metal perchlorates, except for the lithium salt. Conductivity measurements indicate a dissociation constant of 1.00 in water at 25°.[133] Activity coefficients[132] and sedimentation equilibria[134] have been determined. Density and refractive indices of the solid have been measurd.[135] The solid is volatile at low pressures at 200°,[136] undergoes an orthorhombic-cubic transition at 285°, and decomposes above 430° (with an activation energy of 54 kcal/mole) to yield Tl_2O_3 and $TlCl$ (relative amounts depend on both temperature and atmospheric composition).[136,137]

Group IVA Metal Perchlorates. Preparation of either germanium or tin perchlorate has not been reported. Lead perchlorate has been prepared in anhydrous form and as the mono- and tri-hydrate.[138] It is extremely soluble in water, forming a saturated solution at 27° with a density of 2.7753. Use of aqueous solutions of lead perchlorate has been sug-gested for determining densities of insoluble solids by the suspension method.[139] An anhydrous solution of lead perchlorate in methanol is explosive. Basic salts have been prepared by reaction of lead oxide with perchloric acid.[140] Perchlorato complexes of lead have been prepared also,[141] providing the earliest evidence that perchlorate ions can coordinate to metal ions.

Group VA Metal Perchlorates. Antimony oxyperchlorate pentahydrate has been obtained in crystalline form by cooling a solution of freshly precipitated $Sb(OH)_3$ dissolved in warm 70% perchloric acid.[142] The solid compound decomposes above 60° to antimony oxides, and it is dissolved but hydrolyzed by water.

Bismuth perchlorate is prepared as the pentahydrate by reaction of bismuth oxide and perchloric acid.[142] Preparation from metallic bismuth and perchloric acid generally leads to an explosion.[142,143] Bismuth oxyperchlorate can be obtained by hydrolysis of bismuth perchlorate in 40% perchloric acid. Raman spectra have been determined for both $Bi(ClO_4)_3$ and $BiOClO_4$.[126] The crystal and molecular structure of u-oxo-bis(perchloratotriphenylbismuth) have been investigated, indicating that the perchlorate groups are weakly coordinated to bismuth(V).[144]

TRANSITION METAL PERCHLORATES

Much of the interest surrounding the preparation and study of transition metal perchlorates seems to have been focused on three questions: (1) how does the nature of the metal cation influence thermal decomposition of perchlorates?, (2) can advantage be taken of the solubility of metal perchlorates in various solvents to effect separation or other applications?, and (3) to what extent will perchlorate ions coordinate to metal ions? Other than this, the transition metal perchlorates have been explored relatively little. More attention has been given to the solution chemistry of the transition metal ions in the presence of perchloric acid or perchlorates than to the properties of the metal perchlorates.

The crystal structures of the hexahydrates of a number of bivalent metal perchlorates have been determined.[107]

Hexagonal structures, closely related to that of lithium perchlorate trihydrate, are exhibited by the manganese, iron, cobalt, nickel, zinc, and cadmium compounds. Mercuric perchlorate hexahydrate is trigonal, and cupric perchlorate hexahydrate is monoclinic. Infrared spectra of some fully hydrated transition metal perchlorates indicate that the perchlorate group exists in the solids as simple perchlorate ions. For certain lower hydrates, the spectra suggest the presence of coordinated perchlorate groups.[145]

Solubilities in water and other polar solvents are generally appreciable for most metal perchlorates, as exemplified by the data compiled in Table 11. Conductivities and other electrochemical properties of some of the perchlorates in furfural and in Cellosolve have also been reported.[114] Viscosities, densities ,and electrical conductances of 0.001-2 M aqueous solutions of chromium(III), iron(II), thorium(IV), and silver(I) perchlorates at 20°-35° have been determined, also molar refractions and apparent molar volumes of the salts.[120]

A general method of preparing transition metal perchlorates in solution has been described which consists of three main steps: (1) dissolution of a weighed amount of the metal in azeotropic hydroiodic acid, (2) addition of the requisite weighed amount of standard perchloric acid, and (3) removal of the hydroiodic acid by oxidation with ozone followed by volatilization of the iodine formed.[146] In some cases, the simple expendient of dissolving the metal or its hydroxide, oxide, or carbonate is satisfactory. Preparation of the pure solids is frequently complicated by the tendency of the transition metal ions to undergo hydrolysis, yielding hydroxyperchlorates.

Pyridine complexes of a number of bivalent metal perchlorates and silver perchlorate have been prepared and characterized.[85] Hydroxyperchlorates of zinc, cadmium, mercury, and copper have been prepared by dissolving the oxides in solutions of the corresponding perchlorates.[147]

Thermal decomposition studies of some first-row transition metal perchlorates have been carried out by DTA and TGA techniques.[148,149] Stabilities decrease with increasing effective electrical field strength of the metal ion. Activation energies found for the decomposition of $Mn(ClO_4)_3 \cdot 6 H_2O$,

TABLE 11. SOLUBILITY OF METAL PERCHLORATES[114]

Salt	Solubility (g solute/100 ml solvent) in Solvent		
	Water	Furfural	Cellosolve
$Ba(ClO_4)_2$	—	50	100+
$Cd(ClO_4)_2 \cdot 6H_2O$	478	80	145
$Cu(ClO_4)_2 \cdot 6H_2O$	—	70	100+
$Cu(ClO_4)_2 \cdot 2H_2O$	259	20+	—
$Co(ClO_4)_2 \cdot 6H_2O$	292	60	110
$Mn(ClO_4)_2 \cdot 6H_2O$	268	90	130
$Ni(ClO_4)_2 \cdot 6H_2O$	267	60	100+
$Ni(ClO_4)_2 \cdot 2H_2O$	—	20	35
$AgClO_4$	540	40	125
$Pb(ClO_4)_2$	—	25	105
$Zn(ClO_4)_2 \cdot 6H_2O$	—	85	130

$Co(ClO_4)_3 \cdot 3H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, and $Cu(ClO_4)_2 \cdot 6H_2O$ are respectively 21.4, 24.8, 49.0-52.0, and 43.7-45.9 kcal/mole.[149] The hexahydrate of chromic perchlorate undergoes simultaneous dehydration and decomposition to chromic oxide without forming anhydrous chromic perchlorate, and the dihydrate decomposes at 135°-160° with an energy of activation of 17.5 kcal/mole.[150] Bel'kova and coworkers have investigated the thermal behavior of many of the rare earth perchlorates, including determination of their dehydration and thermal decomposition temperatures.[151-153] At 500° all the perchlorates decomposed similarly to give both MOCl and MCl₃ in the solid residue. Thermograms show endothermic effects due to loss of water of crystallization followed by exothermic effects accompanying decomposition of the perchlorate. Most of the hydrated perchlorates lose water gradually up to 200° and begin decomposition in the temperature range 250°-270°. Thermal decomposition is facilitated with increasing polarization effects of the cation. For the trivalent rare earth perchlorates, in the series lanthanum through holmium, increasing atomic number (decreasing cation radius) is accompanied by a decrease in the decomposition temperature.[151] Thermogravimetric studies of the lanthanide perchlorates indicate that dehydration is affected more than the decomposition process by change in applied pressure.[154] Decomposition under non-isothermal conditions yields chlorides. To obtain anhydrous perchlorates it is best to operate at very low pressure and slow heating rates to minimize formation of oxychlorides.

The perchlorate ion was long considered to be a non-coordinating anion and thus ideally suited for avoiding competitive complexation and for maintaining a constant ionic medium in complex equilibria studies. However, findings reported in the early 1960's[145,155,156] and the many investigations that followed have proved this conception false. Vibrational spectroscopy and single crystal X-ray diffraction techniques provided the most convincing evidence of perchlorate coordination. In the absence of strongly coordinating solvent molecules or other ligands, transition metal ions are particularly receptive to perchlorate ion association and complexation. Examples include the ions of chromium,[157] manganese,[158] iron,[159] cobalt,[158-161] nickel,[158-161] copper,[158-163]

zinc,[158,159] mercury,[159] cerium,[159] and thallium.[159] Although quantitative data are lacking in most cases, the perchlorato complexes of metal ions are invariably weak. Labile aquated metal ions are much less prone than inert complex metal ions to form perchlorato complexes of measureable stability. The role of the perchlorate ion as a ligand in solution and the myth of non-coordinating anions have been the subject of recent review articles.[159,164]

Group IB and IIB Metal Perchlorates

Copper and silver perchlorates have been investigated rather extensively, but no studies have been reported of gold perchlorate. Heats of formation of cupric and silver perchlorates in aqueous solutions are —19.0 and —7.75 kcal/mole, respectively. Cupric perchlorate is prepared by dissolving basic copper carbonate in perchloric acid. Its most stable hydrated form is the hexahydrate, which has a m.p. of 82.3°, a water solubility at 23° of 54.3% (density 2.225 g/ml), and a molar heat of solution of —4.6 kcal. Hepta-, tetra-, and di-hydrates have also been described.[131] Silver perchlorate is obtained as a monohydrate on crystallization from aqueous solution and easily converted to the anhydrous form on drying at or above 43°. It is deliquescent, explosive, light sensitive, and very soluble in water. At 0° a saturated aqueous solution of silver perchlorate contains 82.07% $AgClO_4$ and has a density of 2.7251; at 35° it contains 86.21% $AgClO_4$ and has a density of 2.9173.

Silver perchlorate has been reported to explode on pulverizing it in a mortar. In spite of its hazards, silver perchlorate has received considerable attention because of its unusual solubility in organic solvents and ability to form certain addition compounds. It can be used to generate anhydrous perchloric acid in various organic solvents by bubbling dry hydrogen chloride through its solution in the respective solvent. Its solubility in grams per 100 grams of solvent at 25° is 5.28 in benzene, 101 in toluene, 5.28 in aniline, and 26.4 in pyridine. It is also soluble in nitrobenzene, chlorobenzene, glycerine, glacial acetic acid, acetonitrile, nitromethane, and ethyl acetate. It is insoluble in chloroform, carbon tetrachloride, and ligroin. Silver perchlorate is appreciably associated in many solvents.[62,63,114,167] In aprotic sol-

vents of dielectric constant greater than 30 it behaves as a medium-strength electrolyte.[168] In anhydrous hydrofluoric acid, hydrocyanic acid, or polar solvents of high dielectric constant it is extensively ionized. Silver perchlorate has proven useful as a reagent in organic synthesis, as described in Chapter V.

Studies on zinc perchlorate include determination of water vapor pressure of aqueous solutions (0.5 M to saturated) at 0° and 50°,[169] measurement of conductances in the mixed solvent methanol-acetone,[105] determination of osmotic and activity coefficients,[106,170] and measurement of heats of dilution with water and with perchloric acid.[171]

Cell potential measurements indicate that zinc and cadmium perchlorates are completely dissociated in concentrations up to 0.1 M in aqueous solution (in contrast to the non-dissociated halides) and that the mean transport number of the perchlorate ion is 0.595.[172,173] Both zinc and cadmium perchlorates form tetra- and hexa-ammoniates.[174] The dissociation pressure and composition of the zinc compound have been determined as a function of temperature and its heat of formation calculated.[82,175]

Mercurous perchlorate forms a tetrahydrate which can be readily converted to the dihydrate on heating above 36°.[176] In water it can undergo three successive stages of hydrolysis, eventually yielding mercurous oxide. Conductance and potentiometric measurements of highly concentrated solutions indicate abnormal dissociation. Mercury(I) is reported to form a stronger perchlorato complex than mercury(II).[177]

Group IIIB and Rare Earth Metal Perchlorates

Aqueous solutions of scandium, yttrium, and lanthanum perchlorates have been investigated by viscosity and density measurements over the temperature range 25° to 90°. Results indicate that hydration of the cation is weaker the larger its radius.[178] Apparent molar volumes, specific adiabatic and molar compressibilities, and isobaric and molal expansions have also been determined as a function of concentration.[179]

Spedding and coworkers have conducted numerous, extensive investigations of aqueous solutions of rare earth perchlorates. Results reported include densities, equiva-

lent conductances, transference numbers,[180] activity coefficients,[180,181] heats of dilution at 25°,[182] and partial molal heat capacities at 25°.[183]

The solubilities of the lanthanide group metal perchlorates have been determined over the temperature range 25° to 50°. They show very little temperature dependence.[184] Heats of solution of the tetrahydrates in water have been determined also.[185]

Ammoniates[186] and antipyrine complexes[187] of some of the lanthanide group metal perchlorates have been prepared and described. Thermal decomposition of the ammoniates proceeds through several steps, yielding the metal chlorides at 500°.[186]

Neodymium perchlorate hexahydrate has been prepared and dried at 170° to yield the anhydrous solid.[187] Its molar refraction and absorption spectrum in aqueous solution have been determined.[188] Gadolinium perchlorate octahydrate also has been prepared. It is deliquescent and very soluble in water and in alcohol.[189,190]

Several rare earth perchlorates of the actinide group have been prepared: solid uranyl perchlorate,[191] solutions of neptunium(IV), (V), and (VI) perchlorates,[192] and plutonium(III) perchlorate.[193]

Group IVB - VIIB Metal Perchlorates

Preparations of perchlorates of only the first member of each group have been reported. Titanium tetraperchlorate sublimes at 70°, decomposes on aging at 70° in a vacuum, and explodes when heated at atmospheric pressure to about 130°.[194] Anhydrous titanium tetraperchlorate and chromyl perchlorate reportedly contain bidentate perchlorato ligands.[195] Vanadyl perchlorate pentahydrate, $VO(ClO_4)_2 \cdot 5H_3O$, has been prepared by dissolving vanadium(IV) hydroxide in perchloric acid followed by precipitation from 3.5 M perchloric acid.[196] On heating to 140° it loses one water of hydration and is partially oxidized to vanadium(V), at 200° loss of $HClO_4$ occurs, and at 300° formation of vanadium pentoxide takes place exothermically. Absorption spectra of solutions of vanadium(III) and vanadium(IV) perchlorates have been determined.[197] Chromic perchlorate has been prepared in hydrate form containing 3, 5, 6, 9, and 10 moles of

water.[198] Manganese perchlorate hexahydrate is deliquescent, melts at 155°, begins thermal decomposition at 165°, and decomposes rapidly at 230° to manganese dioxide. Its anhydrous salt could not be prepared in pure state.[199] Results of an electron paramagnetic resonance study of manganese(II) in aqueous perchloric acid solutions at 25° and 55° have been interpreted to indicate the presence of an internal monoperchlorato complex, with a stability constant of $(8.0 \pm 1.5) \times 10^{-2}$.[200]

Group VIIIB Metal Perchlorates

Ferrous perchlorate hexahydrate forms long green crystals, is stable in air, loses four molecules of water over 96% sulfuric acid in a vacuum, and is susceptible to air oxidation in aqueous solution.[201] Its solubility in water is 978 g/l at 0° and 1161 g/l at 60°. In ethanol at 20° its solubility is 865.4 g/l. Ferric perchlorate decahydrate loses four molecules of water over concentrated sulfric or phosphorous pentoxide. It is soluble in water to the extent of 1198 g/l at 0° and 1517 g/l at 60°. The existence of perchlorato complexes of iron(III) has received considerable attention by many investigators. Johansson, after a critical review of the literature, concluded that more experimental work of high quality is necessary to settle the issue.[159]

Cobalt(II) and cobalt(III) perchlorates have been prepared, the latter by electrolytic or fluorine oxidation of the former.[202] Anhydrous cobalt(II) and nickel(II) perchlorates reportedly can be prepared either by heating the corresponding hexahydrates below their melting points in a vacuum or by first replacing their water of hydration with dimethoxypropane and then vacuum heating.[203] Hexapyridine complexes of cobalt(II) and nickel(II) perchlorates can be prepared by reaction of the respective perchlorate with pyridine.[85]

Rhodium(III) perchlorate hexahydrate forms light yellow, long needles, is hygroscopic, and has a face-centered cubic structure.[204] Rhodium(IV) perchlorate is dark red and has been prepared only in solution, by dissolving $RhO_2 \cdot 2H_2O$ (obtained as a precipitate by oxidizing $RhCl_3$ in alkaline solution with sodium hypobromite) in 1 M perchloric acid.[205] Palladium(II) perchlorate tetrahydrate has been prepared by dissolving palladium sponge in concentrated nitric acid followed by heating to fumes with 72% perchloric acid.[206] The brown crystalline needles deliquesce in moist air but can be dried over phosphorous pentoxide in a vacuum without loss of the hydrate water.

MISCELLANEOUS PERCHLORATES

Inorganic Perchlorates

Certain non-metallic elements and compounds, notably those of nitrogen, phosphorous and the halogens, enter into chemical combination with perchloric acid and its derivatives to provide a number of interesting inorganic compounds. These are briefly reviewed below.

Nitronium Perchlorate. This compound, also called nitryl or nitroxyl perchlorate, was first prepared by Gordon and Spinks[207] in 1940 by mixing chlorine dioxide with a mixture of ozone and nitrogen oxides generated by passage of dry air through an ozonizer. It has also been prepared by reaction of dinitrogen pentoxide with anhydrous perchloric acid.[208] Nitronium perchlorate is composed of NO_2^+ and ClO_4^- ions,[209] has a very low vapor pressure, is soluble in and recrystallizable from nitric acid, and reacts very rapidly with water to give nitric and perchloric acids with moderate evolution of heat. It reacts vigorously with many organic compounds, explosively with some. Solutions of NO_2ClO_4 in nitromethane or chloroform have been used to nitrate aromatic compounds. Raman spectra of crystalline nitronium perchlorate[210] and of its nitric acid solution[211] have been reported. Thermal decomposition at 100-127° yields, among other products nitrosyl perchlorate.[212] Reaction with metal oxide yields the metal perchlorate.

Nitrosyl Perchlorate. Raman spectroscopy indicates that the compound $NOClO_4$ is composed of NO^+ and ClO_4^- ions.[213] It has an orthorhombic crystal structure,[214] a density of 2.169 g/cc,[215] and a heat of formation of —41.79 $\pm$ 0.08 kcal/mole.[216,217] Reaction with water produces nitrogen oxides. With methanol, nitromethane is formed. Nitrosyl perchlorate reacts violently with many organic compounds. It was first prepared by passing a mixture of nitric oxide and

nitrogen dioxide into 72% perchloric acid followed by fuming to 140° and cooling to crystallize out the monohydrate.[218] The anhydrous salt was obtained on drying over phosphorous pentoxide, first in an atmosphere of nitrogen oxides and then in a vacuum. Its thermal decomposition has been studied extensively, and nitronium perchlorate is one of the products.[219,220]

Hydrazine Perchlorate. The ·hemihydrate, $N_2H_5Cl_4$ $\frac{1}{2}H_2O$, is obtained on neutralization of an aqueous solution of hydrazine with perchloric acid. At or below 60.5° the equilibrium dissociation pressure of the hydrate follows the equation[221]

$$\log P_{mm} = -3047.6/T + 10.98$$

The free energy of dehydration is 1.456 kcal/mole, and the heat of dissociation is 13.95 kcal/mole. The anhydrous salt can be readily recrystallized from ethanol, with a solubility at 60° of 69 g/100g solution and at 0° very slight.[222] It melts at 137-8° and begins to decompose at 145°. Deflagration results if it is heated rapidly. Violent detonation occurs on mechanical impact, shock, or friction.[223]

Phosphonium Perchlorate. A crystalline product, m.p. 46-47°, formulated as $P(OH)_4ClO_4$, has been obtained through the interaction of phosphoric and perchloric acids. Soluble in nitromethane, its conductivity is typical of an ionic salt. Heats of solution and formation in nitromethane are 13.9 and 11.4 kcal/mole, respectively.[224,225]

Selenious Acid Salt. Addition of selenious acid to ice-cold perchloric acid, after warming slightly and then cooling again, yields a crystalline, deliquesent product of formula $Se(OH)_4ClO_4$. In nitromethane, its heats of solution and formation are 4.8 and 11.4 kcal/mole, respectively, and conductivity measurements are indicative of an ionic salt.[225]

Perchloryl Fluoride. The compound ClO_3F undergoes a number of interesting and useful reactions: at 150 to 300° it vigorously oxidizes a variety of reducing agents, with ammonia it forms ammonium perchlorylamide, with aromatic compounds it forms perchloryl substituted compounds, and for certain active hydrogen containing compounds it is an effective fluorinating reagent.[226] Surprisingly stable, per-

chloryl fluoride can be heated in glass to the softening point without etching the surface. Treatment with a concentrated strong base or heating with water at 250 to 300° in a sealed tube is necessary for quantitative hydrolysis to fluoride and perchlorate ions.[227]

Perchloryl fluoride has been prepared by the action of fluorine on potassium chlorate,[228] by electrolylsis of sodium perchlorate in liquid hydrogen fluoride,[229] and by the action of fluorosulfonic acid on perchlorates.[230] Its physical properties have been studied extensively; values reported for some constants include: m.p. —146°, b.p. —46.8°, heat of vaporization 4.6 kcal/mole, critical temperature 95.13°, critical pressure 53.00 atm, critical density 0.637 g/cc, critical molar volume 161 cc, dipole moment 0.023 ± 0.003D, and $\triangle H^0_{f\ 298} = -5.12 \pm 0.68$ kcal/mole.[227,231,232] Thermodynamic properties,[226,233] vapor pressure,[231] surface tension,[232] and viscosity[232] have been measured over various temperature ranges.

The infrared spectrum and fundamental vibration frequencies of perchloryl fluoride have been determined.[227,234,235] The fluorine and three oxygen atoms are bonded separately to the chlorine atom.

Halogen Perchlorates. Fluorine perchlorate, m.p. —167.5° and b.p. —167.5°, has been prepared by reaction of elemental fluorine with 60 to 72% perchloric acid.[236] It is reported to explode always on freezing or when contacted with organic or easily oxidized matter. Chlorine perchlorate, $ClOClO_3$, has been prepared by the reaction at —196° of $ClSO_3F$ with cesium perchlorate or nitrosyl perchlorate.[236] Bromine perchlorate (red liquid, f.p. < —78°) was prepared from the chlorine perchlorate (pale yellow liquid) by treatment with bromine at —35 to —78°.[236] Both halogen perchlorates react at —78° with anhydrous metal chlorides to form metal perchlorates and with gaseous hydrogen chloride or bromide to yield anhydrous perchloric acid and the respective halogen. They also react with fluorocarbon halides to yield novel fluorocarbon perchlorates[237] and with perhaloolefins to form perhaloalkyl perchlorates.[238]

Iodine trisperchlorate has been obtained as a white solid

Organic Perchlorates

Innumerable perchlorate salts of organic bases and chelated metal cations have been reported. Most were prepared as a convenient means of isolating the desired base or cation in a crystalline form of definite chemical composition. Few have been prepared for the purpose of investigating perchlorate chemistry. All show typical perchlorate properties: moderate to good solubility in organic solvents, relatively high conductivity, tendency to decompose at or above their melting point, and the capability of explosive behavior if overheated or detonated by mechanical shock. Representatives of this group are the perchlorates of methylamine,[241] pyridine,[242] benzenediazonium ion,[743] and bis(1,10-phenanthroline)copper(I) ion.[244] Except for the diazonium perchlorates, which are extremely explosive and easily detonated, most perchlorate salts can be handled safely with suitable care.

Aromatic aldehydes, ketones, ethers, and various pyran compounds combine with perchloric acid to form crystalline salts that can be isolated, although they often decompose on storing.[245] Some controversy exists as to whether certain of these should be considered as oxonium or carbonium salts. True carbonium salts, identifiable by their conductivity in nonaqueous solvents and intense color, are formed by the action of perchloric acid on triarylmethylcarbinols or by metathesis of the cloride with silver perchlorate in a suitable solvent.[246,247]

Preparation of the gem-diperchlorate $(CH_3)_2C(OClO_3)_2$ from acetone has been reported, also the gem-diperchlorate of 2-butanone.[248] Alkyl diperchlorates have been prepared from dienes and diols.[249]

Relatively few perchloric esters have been isolated or their physical properties determined because of the severe explosion hazard involved. Meyer and Spormann[250] reported that the methyl ester (b.p. 52°) and the ethyl ester (b.p. 89°) are extremely powerful explosives and that they were unable to avoid explosions in spite of great foresight taken in handling them. Ethyl perchlorate, first prepared by Hare and Boye in 1841,[251] is immiscible with water and slowly hydrolyzed by it. It is soluble in ethanol but still dangerous to handle, because a dilute solution can spontaneously burn completely away if not explode. Preparations reported for other perchlorate esters include those for $ClCH_3CH(OH)CH_2-ClO_4$,[252] $HOC_2H_4OC_2H_4ClO_4$,[252] trichloromethyl perchlorate,[253, 254] acetyl perchlorate,[255] and benzoyl perchlorate.[255]

Perchloryl compounds can be prepared by reaction of perchloryl fluoride with aromatic compounds in the presence of anhydrous aluminum chloride.[256] For example, perchloryl benzene ($C_6H_5ClO_3$, mp.m.$\triangle 3°$, b.p. 232°) has been obtained by this Friedel-Crafts type reaction. It is reasonably stable. Hyrolysis with potassium hydroxide solution produces potassium chlorate and phenol, and nitration with a mixture of concentrated sulfuric and nitric acid yields 3-nitroperchlorylbenzene (pale yellow needles, m.p. 49 to 50°). The relative stability of the perchloryl group towards reductants is evidenced by its ability to remain intact when 3-nitroperchlorylbenzene is reduced with stannous chloride in hydrochloric acid to 3-aminoperchlorylbenzene.[258] Although relatively safe to prepare and use, perchloryl aromatic compounds are sensitive to vigorous shock and high temperature.

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oxymercuration of D-glucal triacetate with mercuric perchlorate has been described by Honda, Dulenko, and Zhdanov.[55]

Solvents

In addition to its use as a solvent for various inorganic reactions and substances, perchloric acid has proven useful as a solvent for certain organic materials, notably cellulose and cellulose derivatives,[56,57] acrylonitrile polymers,[58,59] and crystalline methacrylonitrile polymers.[60]

Perchloric acid can be used alone or in conjunction with other solvent media to selectively dissolve alcohols, ketones, and amines from resinous materials.[61]

The dissolution of fir cellulose by 45-65% perchloric acid has been found to be preceded by formation of addition compounds of the oxonium type.[62] Optimal conditions for formation of addition compounds at 20° are 62 to 65 per cent perchloric acid and 15-min. treatment time. Extensive dissolution of the cellulose occurs with longer treatment. No ester formation was observed.

Explosives, Propellants, and Pyrotechnics

The use of ammonium perchlorate as an ingredient in various explosive mixtures was first described by Oscar Carlson in British and Swedish patents granted in 1897. Since that time various perchlorates have been extensively studied and implemented in a great variety of explosive and combustive devices. Much of the information available on the subject is in the patent literature. Undoubtedly a great deal more is known but restricted to the realm of classified and trade secret information. A brief survey of the uses of perchlorates is provided in the following paragraphs. For further details and literature citations the reader is referred to reviews by Gale and Weber,[63] Kast,[64] Médard,[65] and Girard.[66]

Inorganic perchlorate explosives generally consist of mixtures of either ammonium or potassium perchlorate as oxidant with sulfur and/or various organic materials as fuels. Special additives are commonly present also to modify shock sensitivity, caking qualities, products of combustion, explosive characteristics, bulk density, and water-repellancy. Explosive mixtures that contain potassium perchlorate are

generally less powerful than those with ammonium perchlorate and are suitable for special purposes, such as blasting soft rock and coal deposits. Numerous composite explosives have been investigated, including ammonium perchlorate in combination with other oxidants such as nitrates, nitrocompounds, and organic perchlorates. With a large variety of choices available among oxidants, fuels, and additives, the number of different combinations and compositions that can be formulated is enormous. An almost endless array of composite explosives can be formulated, each with its special advantages and limitations.

Perchlorate explosives afford certain advantages over dynamite and other nitroglycerine explosives. They are safer to handle, less sensitive to shock, considerably less affected by freezing, free from exudation in warm climates, and relatively nontoxic. Their explosive action is somewhat slower and extends laterally more than dynamite, but they are capable of producing relatively greater destructive effects. Perchlorate explosives can be formulated in a great variety of compositions, permitting their adaptation to a wide range of purposes. For example, a suitable choice between explosive compositions enables fragmentation of hard rock into either minute pieces or large blocks.

Organic perchlorates are unique as explosives in as much as the oxidant and combustible material are both present in the same molecule. Consequently, they tend to undergo very rapid reaction and violent explosion when detonated. The perchlorates of guanidine, dicyanodiamidine, aniline, pyridine, methylamine, hydrazine, and metal hydrazines are typical examples.

Ammonium perchlorate is manufactured on a large scale for use in preparing propellant mixtures formulated to undergo relatively slow burning so as to produce nearly uniform acceleration in propulsion of rockets, missiles, airplanes, and other projectiles. Both liquid and solid propellant mixtures are prepared. An example of the liquid kind consists of a suspension of ammonium perchlorate in nitromethane. Solid propellants are basically of two types: composite and homogeneous. The former consist of solid oxidant particles dispersed in a matrix of the fuel; the latter are colloidal mixtures of the oxidizer and fuel in which the

separate phases are not readily distinguishable. Commonly used solid fuels include natural and synthetic polymers, such as polysulfide rubber, hydrocarbon rubbers, epoxy resins, and polyester resins. Composite propellants that contain potassium perchlorate as the primary oxidant generally have higher burning rates, higher flame temperatures, and denser smoke production compared to those with ammonium perchlorate as principal oxidant. Homogeneous or colloidal propellants generally contain a nitrate or nitro compound as the major oxidant and a perchlorate as a supplemental oxidant. Numerous recent patents describe various organic perchlorates as oxidants for use in rocket propellant compositions.[67-75]

Relatively slow burning compositions are required for time fuses, signal flares, and pyrotechnics. Many of the formulations described to date contain one or more metal or organic perchlorates to serve as auxiliary oxidants. Some recently described examples include the use of zirconium perchlorate in pyrotechnical lacquer for primers,[76] ammonium and potassium perchlorates in signal flares,[77] tungsten perchlorate in time delay pyrotechnic compositions,[78] and potassium and titanium perchlorates in firecrackers.[79]

Mixtures of sulfamic acid and ammonium perchlorate have been described in a patent[80] for use in producing a dense smoke or fog. Ignition of an optimum mixture of the two components results in a rapid, self-sustaining reaction yielding hydrogen chloride and sulfur trioxide as combustion products. In the presence of moist air these products absorb water and give rise to a dense cloud or fog-like mist.

Electrolytes

Electropolishing. The technique of electrolytic oxidation is extensively employed to bright polish metal surfaces and to remove surface irregularities in high precision machining of metal parts. In this electrolytic process the metallic sample is immersed in a suitable electrolytic solution and a controlled electric current is passed between the sample as the anode and some suitable metal serving as the cathode. Two important requirements of the electrolyte are that (1) it is not readily oxidized, and thus does not compete with

the oxidation of the anodic sample, and (2) it forms readily soluble salts with the metal ions produced by anodic reaction of the sample to be bright polished. Perchloric acid or its salts possess both of these desirable attributes and thus find frequent application as electrolytes in electro-plating baths. Nonaqueous solutions are most commonly employed, because their use facilitates control of current densities, over-voltage effects, and solubilities.

Among the first to report studies on electropolishing, Jacquet and Rocquet[81] found that iron and steels can be electrolytically polished in a bath consisting of acetic anhydride and perchloric acid, kept below 30°. A d.c. voltage of 50 v., a current density of 4 to 6 amps/dm², and an aluminum cathode were employed. Their procedure was evaluated further by Pellissier, Markus, and Mehl[82] and applied to the electropolishing of tin, aluminum, lead, and alloys of lead and tin. Adjustment of the current density is important in electropolishing in order to prevent evolution of gas at the anode at too high densities or objectionable etching of the sample surface at too low a current density.

Numerous electrolytic solutions have been investigated and applied in electropolishing of metals. Those which contain either perchloric acid or a metal perchlorate in their formulation include the following: (1) acetic anhydride and perchloric acid,[81-84] (2) acetic acid and perchloric acid,[85-87] (3) acetic acid and sodium perchlorate,[88] (4) ethanol and perchloric acid,[89-91] (5) methanol and perchloric acid,[92,93] (6) ethanol, ethylene glycol monobutyl ether, and perchloric acid,[94,95] and (6) dimethylsulfoxide and perchloric acid.[96]

Procedures for bright polishing the following samples have been published or described in patents: aluminum and its alloys,[82-84,88-92] iron and steel,[81,85-88,90,93] nickel and its alloys,[87,95] razor blades,[97] tin and lead alloys,[82] and zirconium and its alloys.[94]

The hazards associated with the use of perchloric acid in electropolishing baths have been emphasized and reviewed by various writers.[98-100]

Voltaic Cells and Batteries. Use of perchlorate salts in electrochemical cells and batteries have received considerable attention in recent years owing to the improved performance, lower concentration polarization, and longer shelf-

life afforded by such electrolytes. Considering the commercial importance of electrochemical devices it is not surprising that much of the information is of a proprietary nature. A brief summary of the literature and patents on the subject is provided in the following paragraphs. The cells are classified according to anode material employed.

Aluminum anode cells, with aluminum perchlorate electrolyte and manganese dioxide cathodes have been described by Schumm.[101] These dry cells are similar to Leclanche dry cells, but they possess relatively low concentration polarization and low activation polarization which compensate for their relatively high internal resistance. Corrosion resistance of aluminum is satisfactory in the presence of the electrolyte buffered at pH 0 to 4; however, gas production and swelling during discharge cause problems in sealing the cells against leakage.

Lead storage cells, employing perchloric acid in place of aluminum is satisfactory in the presence of the electrolyte Cădariu and Schonberger.[103] Although better performance is claimed, some difficulty arises in fabricating lead dioxide adherent electrodes.

Lithium batteries, attractive for their low weight, have been explored extensively. Gaines and Jasinki[104] described lithium - nickel sulfide batteries and their design to improve performance at high discharge rates and at low temperatures. A solution of lithium perchlorate in tetrahydrofuran is employed as the electrolyte in a patented lithium - metallic chromate battery.[105] According to the patent claims, it is light-weight, high in energy density, and both chemically and dimensionally stable. Another battery of high energy density, also patented, is the lithium - copper sulfide battery described by Garth.[106] Its electrolyte consists of a solution of lithium perchlorate in 1,3-dioxolane. A self-sealing battery with a nonaqueous electrolyte was patented by Alder,[107] consisting of a lithium anode, a copper sulfide cathode, and an electrolyte containing by weight 10% lithium perchlorate, 23% 1,2-dimethoxyethane, and 67% tetrahydrofuran. A German patent[108] describes electrolyte solutions of high electric conductance for use in lithium batteries consisting of 1 - 2.5 M lithium perchlorate in mixtures of dioxolane or propylene oxide with 10 to 50% propylene carbonate or ethylene car-

bonate. A lithium-copper sulfide battery, in which the anode chamber containing lithium perchlorate in dimethylformamide is separated by means of a membrane from the cathode compartment containing sodium polysulfide, has been described in a recent German patent.[109]

Magnesium batteries are relatively light in weight and possess high energy densities, especially those that incorporate perchlorate salts as electrolytes. It is reported that a magnesium - silver(II) oxide cell with an electrolyte solution 2.4 M in sodium perchlorate, 1.6 M in lithium perchlorate and 0.1 M in sodium borate can be operated over several weeks at an average discharge voltage of 1.6 volts.[110] A German patent has been granted to Bauer and Winkler[111] for a magnesium - manganese dioxide battery employing a depolarizer containing 7.4 to 24% magnesium perchlorate, 6% carbon black, 2% barium chromate, 0.5% magnesium oxide, and 57% manganese dioxide. Garbacher[112] received a British patent for a high energy density electrochemical cell comprised of a magnesium anode, a cathode of perforated stainless steel coated with sintered nickelous ammonium sulfate and an organic-bound mercuric oxide paste containing carbon black, and an electrolyte of 5 N magnesium perchlorate containing 5% lithium perchlorate incorporated into fibrous carriers.

Various investigators have reported achieving improved performances for zinc - manganese dioxide dry cells (Leclanche cells) by using zinc perchlorate as the electrolyte in place of zinc chloride. For example, significant improvement in retention of capacity at high temperature is claimed.[113] Machat and Sohm[114] found that a Leclanche-type cell with an electrolyte containing 1.5 M zinc perchlorate and saturated with zinc hydroxide provided 4-times the capacity of a conventional Leclanche cell after aging 2 months at 60°. These same authors[115] also found that (1) corrosion of the zinc anode in a Leclanche-type cell is greatly reduced by replacing zinc chloride with zinc perchlorate and (2) the capacity on both continuous and intermittant discharge is improved without loss of other favorable properties. According to Watanabe and coworkers,[116] Leclanche-type dry cells with zinc perchlorate and ammonium chloride as electrolyte give good discharge characteristics under heavy loads.

A zinc - lead dioxide storage cell has been described[117] that contains 40% perchloric acid and resists freezing even at —56°.

Machat and Sohm[118] obtained a patent for a zinc - mercuric oxide battery containing zinc perchlorate electrolyte which is suitable for use in electrical measuring instruments and watches because of its freedom from gas formation.

Perchlorate salts are effective in alkaline electrolytes for preventing passivation of primary and rechargeable cells.[119] For example, calcium perchlorate and sodium hydroxide are employed in an alkaline battery patented by Berger and Dietlin.[120] Tetrabutylammonium perchlorate is employed in nonaqueous electrolyte solutions patented by Katv and Saito.[121]

Miscellaneous. Concentrated perchloric acid is employed in a carbon fuel cell patented by Becker.[122] The cell consists of a carbon cathode in contact with sulfuric acid, a porous clay diaphragm, and a copper or carbon anode in perchloric acid. It operates by oxidation of carbon at 20 to 90°.

A carbon fuel cell utilizing lithium perchlorate and nitrogen dioxide dissolved in a mixture of propylene carbonate and acetonitrile as a nonaqueous electrolyte has been patented by Schlaikjer.[123]

Lead perchlorate has been recommended as a highly soluble salt for use in electroplating and refining of lead.[124,125]

Ozone can be electrogenerated from 40% perchloric acid using platinum anodes refrigerated at —60 to —65°. Yields and current efficiencies improve with increasing current densities and decreasing temperatures.[126]

Animal Feed Additives

Considerable attention has been devoted by Russian investigators to the use of ammonium, sodium, and potassium perchlorates as stimulants for increasing the weight of farm animals and poultry. According to Solun and coworkers, who first reported on the subject,[127,128] the perchlorates exert a significant thyrostatic effect when added to feed rations of cattle and broilers that leads to increased weight gains of up to 20%. The perchlorates are metabolized and completely eliminated, mainly *via* urine, within 24 to 48 hours.

Young bulls fed at a daily rate of 2.5 mg of ammonium perchlorate were found to have gained 19 kg or 17.8% more than controls after 90 days.[129] Their thyroid weights did not change significantly in this time, but some marked differences in microstructure were observed. Similar studies revealed that weight gains depend on feed type.[130-132]

Ammonium perchlorate administered to oxen in their feed increased the deposition of internal fat by 39% and caused a slight but noticeable effect on the aroma of the meat.[133] Ammonium perchlorate administered daily to bulls in their feed over a 7-month period (2.5 mg NH_4ClO_4/kg body weight) resulted in increases in body weights of 17.3 to 20.7%, meat yields of 9.4%, and fat yields of 22.4%.[134] Ammonium perchlorate in the diets of young rams and ewes led to increased weight gains without affecting meat quality.[135]

The effect of ammonium perchlorate on nitrogen metabolism in young chickens has been investigated by Kurilova.[136]

Explosion hazards associated with storage and handling of weight stimulators containing perchlorate salts can be decreased by addition of other salts, according to Yakimenko and coworkers.[137]

Miscellaneous

Anhydrous magnesium perchlorate and barium perchlorate serve as highly efficient drying agents for gases. They are also useful for removing small amounts of polar compounds from inert gases. Further details are described in Chapter IV.

Potassium perchlorate is employed together with strontium azide and boron in a gas-forming composition which is suitable for the rapid inflation of automobile safety bags. Ignition of the gas-forming composition can be rapidly achieved in the event of an automobile collision by use of ignition mixtures of boron, zirconium, aluminum, and/or magnesium with lithium perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, and/or potassium nitrate.[138]

A patented composition to ignite charcoal briquets contains 15 to 16% potassium perchlorate, 4 to 6% metal nitrates, and 78 to 81% carbonized matter.[139]

Use of iron and potassium perchlorate mixtures in the

form of pellets to serve as heat generating material or "thermal reservoir pellets" for initiating action of thermal batteries has been described by Bush.[140,141]

Lead borate glass solder, used for connecting the front and funnel parts of color television tubes, can be selectively dissolved in 0.4 to 1.6 M perchloric acid at or below 85°.[142] It can also be dissolved in 0.5 to 6 M perchloric acid at 21° in the presence of ultrasound.[143]

Perchloric acid has been employed as a drilling agent and disinfectant in the treatment of dental canals,[144] as a component in etching solutions for production of semiconductor devices,[145] and in solutions to passify or prevent corrosion of iron[146] and steel surfaces.[147]

Addition of small amounts of sodium perchlorate to cooling-lubricants employed in machining of metals is reported to reduce friction and increase the wear life of high-speed cutters.[148]

An antipollution system for internal combustion engines has been patented based upon use of oxygen generated by heating lithium perchlorate in the presence of manganese dioxide catalyst.[149] By elimination of air, oxides of nitrogen are eliminated.

Use of aluminum perchlorate in styptic preparations[150] and of diazonium perchlorate in diazo copying compositions[151] have been described in recent patents.

Quaternary ammonium perchlorates have been found useful as sensitizing agents for photographic emulsions.[152,153]

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CHAPTER VII

BIOLOGICAL EFFECTS OF PERCHLORATES

Although ammonium, potassium, and sodium perchlorates exert a number of interesting biological effects in both plants and animals, their toxicities are relatively slight. Nothing in the long history of their manufacture points to any appreciable biological hazard for a worker exposed to them for prolonged periods. According to Levens,[1] who critically review the literature prior to 1960 on the biological action of perchlorates, sodium and potassium perchlorates would be considered to be "slightly toxic" to animals under the classification scheme of Hodge and Sterner.[2] Several other perchlorates, however, are known to be more than slightly toxic. Still others, the great majority, remain to be investigated. In fact, much remains to be learned about the biological modes of action of even the sodium and potassium perchlorates.

ANIMAL STUDIES

Physiological Effects

The effects of perchlorate ions on the thyroid gland and its function in various animals have been extensively investigated. Wyngaarden et al.[3] found that perchlorate produced quantitative discharge of iodide from rat thyroids within 15 min. It proved to be about 10 times more effective than thiocyanate and approximately 300 times more than nitrate. The blocking effect of perchlorate on the collection and retention of iodide by the thyroid may also extend to other iodide-concentrating mechanisms of the animal body.[4] Rats treated with perchlorate for 17 days developed goiters which were hyperplastic and low in iodine.[3] Wyngaarden and coworkers[5] also observed that increasing amounts of iodide, thiocyanate, perchlorate, and nitrate produced marked reductions in the ability of the thyroid glands of rats to concentrate radioiodide. Perchlorate proved to be the most potent anion and nitrate the least. Halmi and Stuelke[6] found that subcutaneous injection of 100 mg or more of sodium perchlorate prevented active uptake of iodine-131 by thyroid glands of rats treated with propythiouracil, a substance known to prevent hor-

mone synthesis involving the combination of tyrosyl groups and iodide ions. According to Krüskemper and Kleinsorg,[7,8] potassium perchlorate interferes with the synthesis of thyroxine in rats and mice. Results obtained by Breslavskii and Simon[9] appear to support this opinion, although contradictory to the conclusions of Wyngaarden and coworkers.[3]

Kleinsorg and Krüskemper[10] studied the effects of thyroxine and antithyroid substances (potassium perchlorate and methylthiouracil) on the serum proteins in rats. Potassium perchlorate fed simultaneously with thyroxine prevented decreases in serum protein. When fed alone at 100 or 250 mg/kg/day, potassium perchlorate raised the β-globulin content by 68 percent in 14 days and 94 percent in 28 days, while the albumin/globulin ratio was lowered from 1.8 to 1.17.

Selivanova[11] found that ammonium perchlorate is as potent as either sodium or potassium perchlorate for inhibiting thyroid accumulation of iodine-131 in rats, mice, and rabbits. Tests with $NH_4{}^{36}ClO_4$ revealed no cumulative toxicity for dogs. Mice gained weight on an ammonium perchlorate treatment of less than 260 mg/kg and lost weight at greater doses.

Kinetics of the distribution of radioactive perchlorate in rat and guinea pig thyroid glands have been studied by Chow and Woodbury.[12] A kinetic analysis of iodide transport in dog thyroid slices by Rochman et al.[13] indicated that 1 m M sodium perchlorate solution inhibited the influx of iodide into the follicles and discharged the trapped iodine-131 into the media with an increased efflux rate.

Mikhailov[14] found that sheep which received 100 mg of ammonium perchlorate per kg weight or 2 mg/kg/day for 6 months with their feed showed decreased protein-bound iodide in the blood, decreased inorganic blood iodide, and increased urinary and fecal iodide excretion. The compound acted directly on the thyroid gland to alter its function. Yamada and Nakamura[15] observed that perchlorate exerts a contracting effect on thyroid glands.

Rousset, Orgiazzi, and Mornex[16] reported that perchlorate ions enhanced thyroid responsiveness in mice to thyrotropin, human chorionic gonadtropin, and long active thyroid stimulators.

Harden and coworkers[17,18] found that perchlorate ions exert an inhibitory effect on the parotid saliva gland. After administration of perchlorate the labial saliva/plasma ratio for iodine-131 decreased 47 per cent from the control value.

Nevelichuk[19] observed antiarrhythmic properties for potassium perchlorate. Given orally to rats each day for 3 days, potassium perchlorate (20 to 910 mg/kg) prevented ventricular fibrillation induced by calcium chloride (i.v.) and decreased the cardiotoxic action of calcium chloride. No relationship between the antiarrhythmic effect and antithyroidal activity was found.

The use of perchlorate as weight stimulators for poultry and farm animals is discussed in Chapter V.

Perchlorate Metabolism

Various studies indicate that perchlorate salts are eliminated in the urine by most animals without chemical reduction of the perchlorate ion. Kerry and Rost[20] recovered perchlorate unchanged in the urine of rabbits administered sodium perchlorate intravenously. Rabuteau[21] recovered potassium perchlorate unchanged in urine of patients treated for malaria. Quantitative recovery of sodium perchlorate from a human subject was reported by Durand.[22] Appearance of sodium perchlorate in urine occured 10 min. after injection. Maximum concentration was observed at about the third hour, and 95 per cent elimination had occured after 48 hr. Eichler[23] observed similar results for the elimination of potassium perchlorate taken orally by man.

Durand[22] discovered sodium perchlorate distributed throughout the entire rabbit body soon after intravenous or intramuscular injection or oral administration. Determined over the time interval of 20 to 130 min. after administration, concentrations of sodium perchlorate were highest in the ovaries, adrenal glands, and urine. Next highest concentrations were found in the spleen, gall bladder, and intestinal mucosa. Concentrations were lower in the heart, liver, kidneys, lungs, brain, blood, gastric mucosa, muscle, bone and testes.

Eichler and Hackenthal[24] found that perchlorate elimination by rats was faster following high than smaller doses, especially during the early hours after administration. Up to 95 to 97 per cent of the perchlorate was excreted in the urine within 60 hr. In a study of potassium perchlorate metabolism in the rat, Goldman and Stanbury[25] found no significant concentration of perchlorate in the kidney, liver, brain, or spleen. They found that the rates of disappearance of the $^{36}ClO_4^-$ radionuclide from the plasma and thyroid and the rate of appearance in the urine were exponential, with half-times of approximately 20 hr. These rates are similar to the disposal rates of ^{131}I found by others.

A comparative study of iodine and potassium perchlorate metabolism in the laying hen revealed that the concentration and distribution properties of the two were very similar.[26] It was concluded that perchlorate may be of value in blocking uptake of iodide into eggs.

Pharmacological Studies

The earliest pharmacological study of perchlorates was reported in 1868 by Rabuteau[21] concerning the use of potassium perchlorate as a therapeutic agent against malaria. Some years later Sabbatini[27] completed a comparative study of the pharmacology of oxygenated chlorine compounds in which he found that toxicity generally decreases with decreasing oxidizing properties. The toxicity of perchlorate, however, proved to be an exception to the rule, being less than that of chlorite but more than that of chlorate. Sabbatini attributed the distinctiveness of perchlorate toxicity to an immobilizaion or diminution effect on potassium ions.

Pharmacodynamic effects of sodium perchlorate on excised muscles and muscular tissues were investigated by Messini.[28,29] Its addition to the perfusion fluid produced muscle contractions that could be relieved by small amounts of potassium chloride, smaller than that required to inhibit muscle excitability. Washing with sodium chloride enabled the sequence of contraction and relaxation to be repeated. Reversing the order of treatment produced the reverse change, i.e. increased muscle tone from high doses of potassium chloride was diminished by sodium perchlorate. Messini attributed these phenomena to a disturbance of potassium ion equilibrium within the muscle.

From investigations on the reactions of transversely striated muscle (frog sartorius) to sodium and potassium per-

chlorates and other salts, Boehm[30,31] concluded that the contractions produced by perchlorate and fluoborate anions were both related to precipitation of albumin within the muscle.

Adding to the controversy regarding the cause of muscular contractions induced by perchlorates, Eichler[23] reported that perchlorate-poisoned frog hearts were cured by addition of calcium ion but not by potassium, indicating that the poisoning was more akin to an excess rather than a deficiency of potassium. On the other hand, both Cartolari[32] and Spagnol[33] reported pharmacodynamic studies leading to the conclusion that the contraction effect of perchlorate on muscles is produced by decreasing the potassium ion balance.

Hypothyroidism has been successfully controlled in human patients by treatment with oral doses of potassium perchlorate.[34-37] In general, symptoms improved, basal metabolisms fell to nearly normal, body weights increased, and blood cholesterol levels increased to normal values. No significant changes in the formed elements of the blood nor evidence of liver damage were observed for patients treated for as long as 52 weeks.[35]

Brügel[38] found that perchlorate inhibited accumulation of iodine-131 in human subjects to the extent that less than 1 per cent of the normal amount was taken up. According to Lewitus,[39] perchlorate ions compete with inorganic iodide in the trapping mechanism of the thyroid gland, leading to decerased throxine synthesis.

Toxicology and Pathology

Symptoms of perchlorate poisoning in various animals have been described by Kerry and Rost.[20] Frogs injected with 0.015 to 0.030 g of sodium perchlorate exhibited fibrillation, twitching, and strong contraction of transversely striated muscle radiating from the injection site. Reflex excitability was greatly heightened, and heart action was gradually paralyzed. Symptoms were less severe when sodium perchlorate was administered orally, and the frogs recovered completely from oral doses of less than 0.15 g. Similar symptoms (convulsions, paralysis, and rigidity) were observed for sodium perchlorate poisoning in mice, rats, guinea pigs, pigeons, cats, and dogs. Subcutaneous doses of 0.025 g of sodium perchlorate were lethal to mice, 0.22 g to rats, and

1.35 g to guinea pigs. Relatively large oral doses (1 to 2 g) proved fatal to a guinea pig and a rabbit but not to a cat or a dog.

Kahane[40] found that goldfish were unaffected after 3 days in 0.1 per cent sodium perchlorate solution, but that exposure to higher concentrations (0.2 to 2 per cent) resulted in their death. No evidence of reduction of perchlorate to either chlorate or chloride was found.

Leeches immersed in 0.5 per cent sodium perchlorate solution were unharmed after 5 days; two-thirds died after 2 days in 1 per cent solution; and all expired in a 4 per cent solution within 1 hr.[22] Tadpoles were affected after 48 hr in 0.1 per cent sodium perchlorate solution, and in 0.2 per cent solution all died within 36 hr.[22]

The toxicity of sodium perchlorate in rabbits has been investigated extensively by Kahane[40] and by Durand.[22] Autopsies performed on rabbits subjected to repeated injection of sodium perchlorate revealed no evidence of changes in the heart, kidney, or intestines. However, necrosis of the tissue at injection sites, caseation of the liver, and hepatization of the lungs were evident.

According to Selivanova,[11] the minimum lethal dose of ammonium perchlorate is 3.5 g/kg for rats, 2 g/kg for mice and 0.75 g/kg for rabbits.

The general toxic effects of perchloric acid when administered orally or sub-cutaneously to rats, mice, and dogs have been described in detail by Selivanova and coworkers.[41] In addition to its acidic irritating effect, perchloric acid produces a specific antithyroid action and induces abnormalities in hepatic, renal, cardiovascular, and hemapoietic functions when administered internally.

Perchloric acid is reported to cause dermatitis if permitted to act directly on the skin in sufficient amount or concentration for a sufficient length of time.[42,43] Although its corrosive or irritating action is not as immediate nor quite as damaging as concentrated nitric, sulfuric, or hydrochloric acid, due caution should be followed in handling it to avoid contacting it with the eyes and skin. In the event of accidental contact the affected area should be washed immediately with large quantities of water. Prompt medical attention should also be received after any contact with the eye.

The inhalation toxicity in rats and mice of the combustion products of rocket propellants containing various amounts of perchlorate has been investigated by Feinsilver, Mac Namee, McGrath, and Oberst.[44]

Toxicological effects of perchloryl fluoride in rodents and dogs have been studied by Kunkel and coworkers.[45,46] The subject also has been reviewed in detail by Levens.[1]

BACTERIAL AND MICRO-ORGANISM STUDIES

Chemical reduction of perchlorate to chloride ions by several species of heterotrophic bacteria has been demonstrated with the use of chlorine-36 labelled perchlorate by Hackenthal and coworkers.[47] The reduction is strictly dependent upon the presence of bacterial nitrate reductase. Perchlorate reduction by Staphylococcus epidermidis in complex media is inhibited by nitrate, and nitrate reduction of resting cells of Bacillus cereus is inhibited by perchlorate. These results suggest that nitrate and perchlorate ions may be substrates to the same enzyme, nitrate reductase. The rates of reduction of both anions are equally dependent on pH, incubation temperature, and several electron donor and cofactors.[48] Moreover, both activities are inhibited by cyanide, azide, and 2,4-dinitrophenol, as well as by one another in a competitive manner. Perchlorate is reduced first to chlorate and then to chloride by cell-free extracts obtained from nitrate-adapted cells of B. cereus. Hackenthal and Arbabzadeh[49] also found that nitrate reduction in cell-free extracts from B. cereus and Pseudomonas aeruginosa is competitively inhibited by perchlorate, thiocyanate, selenocyanate, chlorate, rhenate, and azide.

The toxicity of aqueous solutions of sodium perchlorate to Escherichia coli and other micro-organisms has been described by Durand.[22] Development of E. coli and of Staphylococcus pyogenes aureus is prevented by concentrations of about 2.5 to 3.0 and 7.5 to 10 per cent, respectively. For the mold Sterigmatocystis nigra development is retarded by a concentration of 1.3 and arrested by a 10 per cent solution of sodium perchlorate.

Sodium perchlorate has been found to affect both the respiration and enzymatic activity of soil micro-organisms.[50] In either incubated soil or pure cultures of soil bacteria, sodium perchlorate inhibited the respiratory activity and decreased the number of ammonifying, nitrifying, and denitrifying bacteria. According to Karki and Kasier,[50] the perchlorate acted in 2 ways: by altering metabolites that are toxic to the cells and by competing with nitrate for the nitrate-reductase A enzyme.

Ammonium perchlorate solutions of concentrations 0.5 to 2 mg/ml are reported to have cytostatic or lethal effects on Paramecium caudatum, Saccharomyces cerevisiae, and Candida tropicalis.[51]

PLANT STUDIES

Numerous investigations have been devoted to characterizing the action of perchlorate on plants, prompted in large measure by findings in 1896 by Sjollema[52] that Chile saltpeter contains potassium perchlorate as a contaminate (in amounts ranging from 0 to 6.79 per cent) which can cause damage to plants. The early studies clearly demonstrated that certain levels of sodium or potassium perchlorate were harmful to plants; however, some doubt arose as to whether or not Chile saltpeter normally contains sufficient perchlorate to be injurious to plants if used in fertilizers.[53,54] Sjollema[55,56] pointed out that the sporadic nature and irreproducible results observed for crop damage attributable to use of Chile saltpeter could be accounted for by the fact that potassium perchlorate is not uniformly distributed in the mineral but occurs in pockets. He also observed that certain suppliers had begun (in about 1892) to recycle the saltpeter mother liquor excessively, which could account for a build-up of perchlorate content and the sudden appearance of damage to crops. In 1914, Maschhaupt[57] reported finding a maximum perchlorate content of 1.5 per cent in crude and about 1 per cent in refined saltpeter; in fertilization experiments these levels inhibited plant growth, confirming the findings of Sjollema. More recently, Tollenaar and Martin[58] found that potassium perchlorate in Chilean nitrate was responsible for stunted soybean plants in Chile. The plants were 50 to 67 per cent reduced in size and bore strongly crumpled leaves with burned tips. Clearly there is a need

for careful quality control in processing and selecting of Chilean saltpeter for use in fertilizers.

Considering the possible implications to marine vegetation, a 1958 report[39] that perchlorate had been found at 10 to 1000 ppm concentrations in sea water from various localities attracted considerable attention. Extensive and thorough testing by others[60-64] failed to substantiate the claim that perchlorate is an important constituent of sea water. Greenhalgh and Riley[61] attributed the alleged finding of perchlorate to chloride ion interference in the analytical method.

The major action of moderate concentrations of perchlorates on plants is inhibition of growth. Seed germination is also retarded or terminated. Various studies substantiate these general conclusions, at least with regard to plant species studied thus far. Sjollema[52] observed that rye plants grown in pots containing as little as 50 mg of sodium or potassium perchlorate were stunted and bent and bore yellow leaves. Exposure to perchlorate delayed germination of rye seeds and resulted in abnormal embryos. Growth retardation of rye and oats by perchlorates was reported by Maercker[65] and by Caluwe.[66] Lauffs[67] found small amounts of perchlorate to be beneficial to growth but large amounts to be toxic to wheat plants. Root hairs of wheat plants grown for 8 days in dilute perchlorate solution were deformed.[67] Exposure of young wheat and rye plants to 0.2 to 1.0 per cent potassium perchlorate for only a few hours, however, had little effect on root hairs.[68] Ekdahl[69] confirmed these findings by similar experiments with root hairs of young wheat plants grown in water culture. He also found that the toxicity of various chlorine compounds decreased in the following order: hypochlorite, chlorite > perchlorate > chlorate > chloride. Åberg[70] observed, however, greater toxicity for chlorate than for perchlorate in studying the effects of a number of salts on young wheat plants grown in nutrient solution.

The toxicity of perchlorates vary with the type of plant, culture or soil in which the plant is grown, and lighting conditions to which the plant is exposed. The relative toxicity of perchlorate to chlorate apparently may vary also, or even be reversed, from one set of conditions to another. Weaver[71] found that perchlorate was more toxic to Biloxi soybean plants grown in water culture than to those grown in sand; he found the opposite to be true for chlorate. Åberg[70] observed that root injuries to young wheat plants occurred when they were grown in nutrient solution containing 0.5 mmol/l potassium perchlorate, but only for lightgrown plants. Those grown in darkness under similar conditions withstood damage. Cook found that perchlorate is more toxic than chlorate when sprayed on plants grown in soil,[72] even though in solution culture the lethal dose to the plants is about the same (0.25 per cent) for both anions.[73] Perchlorate and chlorate both caused mottling of leaf foliage in young tomato plants, but with different characteristics, in experiments reported by Owen.[74]

Alvisi and Orabona[75] observed that solutions of potassium perchlorate were initially harmful but eventually beneficial to bean plants. With ammonium perchlorate, the anion appeared to be decomposed by the bean plant, while potassium perchlorate was unchanged. Similarly, *Penicillum glaucum* reduced ammonium perchlorate but not potassium perchlorate. Treatment of a 0.2 per cent potassium perchlorate solution with pepsin, papain, or diastase for 1 to 6 days at room temperature failed to produce detectable chloride ion levels.

Weiske[54] found that germination of grains and vegetables was retarded by exposure of the seeds to potassium perchlorate. Germination of the seeds of *Pisum sativum* was only slightly decreased by soaking 24 hr in 1 per cent potassium perchlorate, according to Vandevelde.[76] In experiments conducted by Durand,[22] seeds of poppy, lentil and flax germinated almost normally in 0.2 per cent sodium perchlorate, but they were affected appreciably in 0.5 per cent solution.

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CHAPTER VIII

SAFETY AND ENVIRONMENTAL CONCERNS

Those who would employ perchloric acid or perchlorate compounds to good advantage in any of the many and valued applications known for these substances should be mindful of the hazards involved. There resides in most perchlorates an awesome oxidation power which, if unleashed in force upon oxidizable matter, can give rise to conflagrations or fierce explosions. Although calamity awaits anyone who would use a source of power carelessly, there are sensible and safe methods available to harness and control power for useful purposes. In the case of perchlorates, the essential guidelines for safeguarding against unleashed power and havoc involve the following measures: (1) control of both temperature and concentration, (2) exclusion of certain substances from contact with perchlorates to prevent reactions that produce unstable perchlorates, and (3) minimization of amounts of oxidizable matter that can come into contact with any perchlorate at any one time. The ferocity of the oxidation power of perchlorates thus can be controlled as needed in any application.

Specific precautions and safety measures in handling and storing perchloric acid and perchlorates are summarized in the following sections. For a clearer understanding of the risks and safety measures, the properties of perchloric acid and of the perchlorates should be reviewed in Chapters II, III, and VII. Other sources[1-4] may also be consulted.

Some Reported Perchlorate Explosions

Reports of early investigators attest to the fact that anhydrous perchloric acid is not only exceedingly corrosive to the skin and mucous membranes but explosively unstable.[5,6] It should not be prepared except for special needs nor stored except at low temperature and then only in small quantities and for short periods.[5-7] The monohydrate, although considerably more stable and storable for long periods in sealed glass ampoules without discloration,[7] can react explosively with organic matter.[5,8]

Explosions have been reported for various perchloric acid mixtures. The most tragic was that which caused the death of 17 persons in Los Angeles, California, on February 20, 1947. It apparently occurred as a result of the introduction of a plastic holder into an electropolishing mixture consisting of approximately 150 gal. of 68-72% perchloric acid and 20 gal. of acetic anhydride, contained in a stainless steel tank (phenolic resin-coated) and fitted with a refrigeration system that had been shut off.[9,10] The unfortunate combination of elevated temperature, concentrated perchloric acid, and reactive organic matter resulted predictably in the inevitable. Other mixtures for which explosions have been reported on subjection to high temperature include those with aqueous perchloric acid and the following: alcohols,[11,12] hydrogen,[13] wood,[14] acetic anhydride (containing more than 57% by volume $HClO_4$),[15] bismuth metal,[16] easily oxidizable organic materials,[17] sodium hypophosphite,[18] sulfoxides,[19] phenol,[19] and various wet-oxidation mixtures which were not adequately preoxidized by treatment with nitric acid[20-22]

It should be emphasized that aqueous perchloric acid solutions of concentration 72% by weight or less are remarkably stable to heat and shock, provided that reactive material is absent. For example, Dietz[13] reported that boiling 72% perchloric acid could not be detonated when primed with mercury fulminate or lead azide. Introduction of an electrical arc into the boiling acid produced only weak, local deflagrations.

Some of the most hazardous perchlorate compounds reported are those that are most sensitive to heat or shock. They include the highly explosive diazonium perchlorates,[23] silver perchlorate,[24,25] hydrazine perchlorate,[26] fluorine perchlorate,[27] and perchlorate esters of aliphatic alcohols.[28-31] Other perchlorate compounds for which explosions have been reported on heating or by detonation are the following: aniline perchlorate,[32] pyridine perchlorate,[33] benzyl perchlorate,[34] silver perchlorate-benzene complex,[35] dimethylamine perchlorate,[36] tris(ethylthio)cyclopropenylium perchlorate,[37] and 1,3-dithiolium perchlorate.[38] The perchlorates cited here serve only as examples; they certainly do not constitute a complete list of hazardous perchlorates. It is both reasonable and wise to assume that all organic perchlorate and most heavy metal perchlorates are capable of explosive decomposition under certain conditions. There is no substitute for cautious experimentation guided by diligent attention to lessons from the past.

Precautions in Use and Handling of Perchloric Acid

Various agencies, organizations, and individuals have formulated recommendations concerning the handling, storage, and dispensing of aqueous perchloric acid. These include the Manufacturing Chemists' Association,[39] the National Safety Council,[40] the Factory Mutual Engineering Division,[41] the Association of Casualty and Surety Companies,[42] the Association of Official Agricultural Chemists,[43] the Analytical Methods Committee of the Society of Analysts,[44] Harris,[45] Muse,[3] Gawen,[46] the National Fire Protection Association,[47] and Everett and Graf.[48] Many of these rules and recommendations are summarized below. However, as emphasized by Levens,[2] the prospective user should not rely unquestioning only on rules but rather should "first become familiar with the properties of perchloric acid, and then, for each case, give the most careful consideration to the proposed experimental conditions and operating procedure." Some of the most important properties of perchloric acid in this regard are therefore also cited in the list of precautions that follows:

1. Anhydrous perchloric acid is extremely unstable and will explode spontaneously. Its preparation should be avoided.

2. Aqueous perchloric acid in concentrations less than 85% is completely stable under ordinary storage conditions. The concentrations normally supplied commercially are 60 and 72%

3. Boiling or evaporation of an aqueous solution of perchloric acid will not produce a dangerously high concentration because an azeotropic mixture results which at 760 mm pressure contains 72.5% $HClO_4$ and boils at 203°C. If metallic salts are present, however, the mixture should not be evaporated to dryness over an open flame.

4. The dangerously explosive anhydrous acid may form accidentally if the aqueous acid is subjected to strong dehydrating conditions, such as provided by hot, concentrated sulfuric acid or phosphorus pentoxide. Special care is required